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Enhancement of Raman scattering by field superposition of rough submicrometer silver particles

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Wavelength-dependent surface-enhanced Raman spectra of methylene blue adsorbed on rough submicrometer silver particles were measured. Results revealed a high enhancement factor ($10^5 \sim 10^7$), especially in the long-wavelength region. Investigation on the far- and near-field optical properties of the particles showed a remarkably enhanced dipole plasmon resonance due to the presence of a rough particle surface. Through analyzing the plasmon resonance modes and the superposition of radiation fields, we found that the rough surface-induced field superposition results in the redistribution of optical fields around the particle, which becomes a key factor responsible for the high enhancement effect of metal particles. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4705083]

Submicrometer particles of noble metals, such as gold and silver, are showing promising applications in various hi-tech fields.[1–4] These metal particles show distinctive optical properties in the visible and near-infrared region,[5] which are attributed to collective oscillations of the conduction electrons, known as the localized surface plasmon (LSP).[6–8] The LSP resonance frequencies of metal particles rely on their size, shape, composition, and surrounding medium.[9] Extensive experimental and theoretical investigations have shown that metal particles of less than 100 nm exhibit optimal local field enhancement effect,[10–12] while further increasing the particle size will decrease this effect.[13] However, contrary to this trend, the recent preparation of a series of submicrometer metal particles with nanoscale surface roughness represents the discovery of a class of materials with distinctive field enhancement capability.[14–17] For example, using meatball-like gold particles as the substrate, Halas and coworkers performed surface-enhanced Raman scattering (SERS) measurements and obtained a high enhancement factor (EF) of 10^7.[14] Significantly increased SERS intensities using flower-like silver particles were also recorded.[15] These studies revealed that the high enhancement originates from the local fields of the nanometer-scale protrusions and crevices on the randomly textured surface.

It is generally accepted that the enhancement effects are credited to the presence of hot spots on the rough particle surface. But a recent publication inspired us to think other possible mechanisms that can also contribute to the Raman enhancement. In the paper, Bok *et al*. reported an intraparticle surface plasmon coupling in Au nanorod structures with a heterogeneous surface morphology.[18] Following this concept, it is reasonable to question if there is a field superposition between the inner core and the surface protrusions of rough submicrometer metal particles. In the present contribution, we perform experimental and theoretical investigations toward elucidating the role of field superposition in the optical properties of rough submicrometer metal particles.

Submicrometer silver particles with distinct surface protrusions were prepared according to the literature,[15,19] and characterized by scanning electron microscopy (SEM). Estimated from the SEM image (Fig. 1(a)), the average grain size of the silver particles is about 500 nm. The Raman spectra of methylene blue (MB) adsorbed on rough submicrometer silver

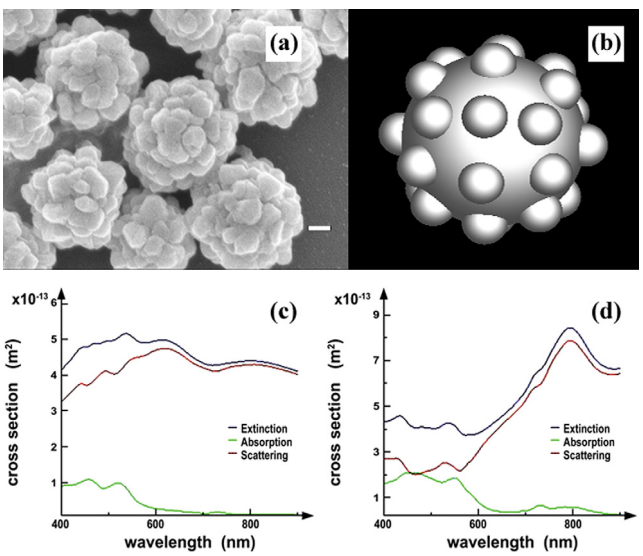

FIG. 1. (a) The SEM image of rough submicrometer silver particles. Scale bar: 100 nm. (b) Schematic diagram of the rough submicrometer silver particle model. The 26 small peripheral particles were submerged into the large core particle, effectively generating many hemispheres on the surface. (c) Calculated extinction, absorption, and scattering spectra of the smooth silver particles model. (d) Calculated extinction, absorption, and scattering spectra of the rough silver particle model.

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particles was measured.[19] As defined in the references,[20,21] Raman EF was calculated by using

$$EF = \frac{I_{SERS}/N_{SERS}}{I_{RS}/N_{RS}}, \quad (1)$$

where I_{SERS}/N_{SERS} is the SERS integrated intensity of some typical band reduced to a single adsorbed molecule, and I_{RS}/N_{RS} the corresponding spontaneous Raman intensity of the same band. The EF calculation results are 3.2×10^5 and 1.3×10^7 for SERS excited by a 514.5 nm Ar-ion laser and a 785 nm diode laser, respectively. Given that the EF is directly associated with the optical properties of the metal particles, we thus consider the use of extinction spectra to help us understand the results from the SERS experiments. For a comparison study, it will be preferable to prepare submicrometer metal particles with a perfectly smooth surface. However, it is not experimentally feasible. Therefore, as an alternative way, we carry out theoretical simulation works.

Three-dimensional finite difference time domain (FDTD) method was employed to calculate both far- and near-field optical properties of submicrometer silver particles.[19] Based on the SEM image of the experimentally synthesized particles, a rough silver particle model was constructed (Fig. 1(b)). This model contains 26 small spherical particles ($D = 100$ nm) evenly distributed on the exterior surface of a large particle ($D = 400$ nm). A spherical particle ($D = 400$ nm) with a perfectly smooth surface is used as a smooth model. Calculated extinction, absorption, and scattering spectra of the smooth and rough silver particle models are shown in Figs. 1(c) and 1(d), respectively. The extinction spectrum of the smooth particle model is featured by a broad band originated from dipole resonance (~800 nm) and also higher-order multipole resonances, such as quadrupole resonance (~620 nm).[22,23] Contrary to Fig. 1(c), an intense peak centering at ca. 800 nm appears in the extinction spectrum of the rough particle model (Fig. 1(d)). This indicates a serious dipole field intensification, which is mainly contributed by the scattering. For the above-mentioned wavelength-dependent SERS measurements, the two excitation wavelengths correspond to the multipole and dipole plasmon resonance peaks of the metal particles, respectively. Consistent with the extinction spectrum in Fig. 1(d), the rough silver particles show a higher EF by 785 nm excitation, compared with 514.5 nm excitation. The distinct variation of EF also supports our simulation results that the dipole peak of rough silver particles would be enhanced after illumination.

Previous results have shown that the rough surface would enhance the dipole field for the extinction spectrum of metal particles. For the enhancement effect, the LSP resonance of metal particles is primarily responsible for the results of SERS experiments, suggesting the connection of local fields between the surface structure and the particle. To gain a deeper physical insight into the wavelength dependence of SERS, the distribution of electric fields of metal particles was also calculated using FDTD. Figs. 2(a) and 2(b) show the near-field plots for the smooth silver particle model illuminated with 785 and 514.5 nm light, respectively. The excitation field is incident in the positive z direction and polarized along the x-axis. Typical dipole field enhancement

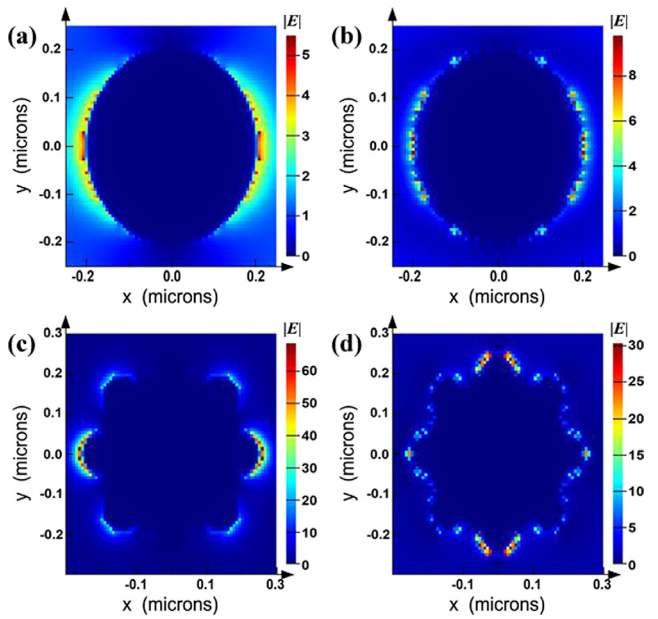

FIG. 2. The distribution of electric fields around the silver particle model calculated by FDTD. (a) and (b) The smooth silver particle model excited by 785 and 514.5 nm, respectively. (c) and (d) The rough silver particle model excited by 785 and 514.5 nm, respectively.

is obtained as shown in Fig. 2(a). The near-field enhancement in Fig. 2(b) is a multipole mode, which should arise from mixing of the octupole component and the quadrupole component as a result of retardation. Figs. 2(c) and 2(d) show the near-field plots for the rough silver particle model illuminated with 785 and 514.5 nm light, respectively. Compared with Figs. 2(a) and 2(b), there is a remarkable near-field enhancement of the rough silver particle. It has been pointed out that the electric field surrounded the particle is determined by the applied field and the polarized field resulted from polarization of the conduction electron density.[24] The rough surface leads to a more localized distribution of the particle's conduction electrons. Therefore, the local field of the particle was redistributed based on that of the smooth particle, and the electric field intensity on particle surface was also elevated.

The extinction spectra calculated previously show that the presence of a rough surface remarkably increased the dipole peak intensities. To assist our understanding of the radiation field superposition phenomenon, a mathematical analysis based on the rough particle model is performed. We consider that the overall observed LSP radiation originates from both the large core particle and small peripheral particles. Therefore, the radiation field superposition between the dipole or multipole of the core particle and the dipole of the peripheral particles can be expected. According to the superposition principle, the overall electric field equals to the sum of radiation fields from the core particle and peripheral particles. If the overall electric field is denoted by the vector $\mathbf{E}$, we have

$$\mathbf{E} = \mathbf{E}_0 + \sum_{i=1}^{n} \chi_i(r_i)\mathbf{E}_i, \quad (2)$$

where $\mathbf{E}_0$ and $\mathbf{E}_i$ are the radiation fields, respectively, produced by the LSP resonance of the core particle and peripheral particles, n is the number of the peripheral particles, and

$\chi_i(r_i)$ is the weighing factor with r_i, a parameter defining the position of the peripheral particles. Considering the local field of the rough particle is redistributed from those of the smooth particle, χ_i is determined by the E_0 at r_i.

To achieve electromagnetic field enhancement through coherent superposition, certain conditions should be met. Under the same excitation wavelength, electrons of a metal particle oscillate with the same frequency. For an excitation wavelength of 514.5 nm, the plasmon resonance mode for the large core particle is multipolar. In this case, collective electron oscillations are not only parallel but also perpendicular to the direction of the incident light. Therefore, the polarization direction of the radiation field is not solely parallel to the polarization direction of the incident light. However, for the dipolar plasmon radiation originated from the peripheral particles, the polarization direction of the radiation field is parallel to the polarization direction of the incident light. Due to the difference of polarization directions, there is no coherent superposition of the radiation fields. On the contrary, when the 785 nm excitation light is used, the plasmon resonance mode of the core particle becomes dipolar. In this case, electrons from both the large core particle and small peripheral particles oscillate in the same direction. Since the positions of the peripheral particles are fixed, the phase difference of the radiation fields is kept constant making coherent superposition of the radiation fields possible. Therefore, Eq. (2) can be simplified to a scalar equation.

Based on the equation of the radiation field produced by the dipole resonance, we have

$$E_0 = \frac{k^2 P_0 \sin\alpha}{4\pi\varepsilon_0 r} e^{ikr}, \tag{3}$$

where ε_0 is the vacuum permittivity, P_0 is the dipole moment of the large core particle, k is the wavenumber of the radiation field, α is the angle between the incident and radiation fields. As illustrated in Fig. 3(a), for a certain radiation direction **r**, there will be a constant phase difference between the radiation waves of large core particle and small peripheral particles. The phase difference is $R\cdot\cos\theta\cdot(2\pi/\lambda)$. Therefore, E_i can be written as

$$E_i = \frac{k^2 P_i \sin\alpha}{4\pi\varepsilon_0 r} e^{ik(r+R\cos\theta_i)}. \tag{4}$$

For any E_i and E_0, we have

$$E_{Total}^2 = E_0^2 + \chi_i^2 E_i^2 + 2\chi_i E_0 E_i \cos(kR\cos\theta_i). \tag{5}$$

For a dipole radiation field at 800 nm, the above-mentioned phase difference will always be less than $\pi/2$, which indicates an elevation of the overall electric field, $E_{Total} > E_0$. As a result, there is a remarkable enhancement of the dipole LSP resonance in the extinction spectrum of rough submicrometer silver particles, while no notable change of the higher-order multipole LSP resonance is observed.

For the small peripheral particles, the induced dipole moment is correlated with the particle size[24]

$$P = E_{ex} a^3 \frac{\varepsilon_{np} - \varepsilon_0}{\varepsilon_{np} + 2\varepsilon_0}, \tag{6}$$

where a is the radius of the particle, E_{ex} is the exciting electric field, and ε_{np} and ε_0 denote the relative permittivity of the particle and the surrounding medium, respectively. Thus, for a submicrometer particle with nanoscale surface roughness, the dipole enhancement is associated with the grain size of the surface protrusions. In a further test, we altered the diameters of the peripheral particles of the model, and calculated the extinction spectra. As shown in Fig. 3(b), results show that dipole radiation field intensity increases as the peripheral particle size increases.

To verify the results of the electric field by theoretical simulation, the intensity distribution of optical fields of the rough submicrometer silver particles on a quartz slide was measured by near-field scanning optical microscopy (NSOM), under 785 nm excitation (Fig. 4(a)). As a comparison, spherical silver nanoparticles with 90 nm diameter were also been measured (Fig. 4(b)). As can be seen, the rough submicrometer silver particle shows a strong optical field distribution. The field strength is significantly stronger than the spherical nanoparticles supporting a pronounced enhancement effect. Near-field observation visually confirms the effects of the surface structure on the optical properties of metal particles.

In summary, we explored here the effects of a rough surface on the variations of far- and near-field changes of submicrometer silver particles. An increase of EF was recorded when excited by 785 nm laser light comparing to the 514.5 nm excitation. FDTD calculation showed that the dipole-dipole field superposition between the large core particle and small peripheral particles contributed more to the Raman enhancement than the quadrupole-dipole field superposition. This contribution employs the concept of intraparticle polarized field superposition to explain the optical properties of rough submicrometer particles. We expect that

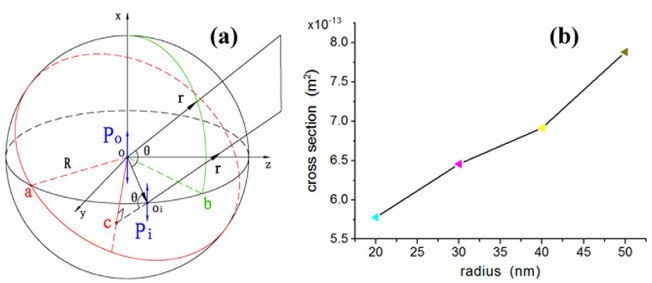

FIG. 3. (a) Schematic plot of field superposition effect of the rough silver particle model. (b) Dipole LSP resonance enhanced by increasing the radius of the peripheral particles.

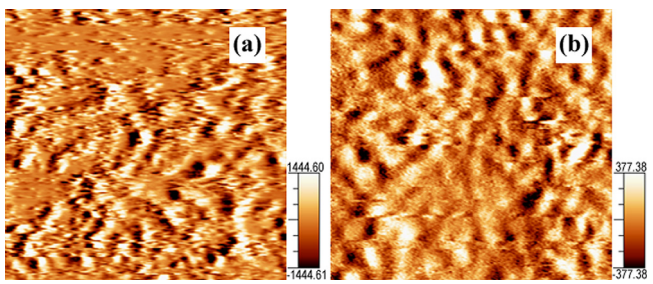

FIG. 4. The intensity distribution of optical fields measured by NSOM under 785 nm excitation. (a) Rough submicrometer silver particles. (b) Spherical silver nanoparticles.

this methodology could be applied to different submicrometer material systems with heterogeneous surface morphology.

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