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Emission pattern of surface-enhanced Raman scattering from single nanoparticle-film junction

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Emission pattern of surface-enhanced Raman scattering (SERS) from the junction of single nanoparticle and a metal film was experimentally demonstrated. The presence of a thin metal film enables the excitation of surface plasmon polaritons (SPPs) to greatly improve the excitation efficiency of SERS, which is subsequently coupled back to SPPs and re-radiates into the substrate side with higher refractive index at SPP excitation angle. The so-called surface plasmon coupled emission can serve as a high sensitivity detection tool for SERS and particularly for the tip-enhanced Raman spectroscopy. © 2013 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4793667>]

Surface plasmons (SPs), the coherent oscillation of free electrons excited by electromagnetic radiations,¹ played a remarkable role in the area of nanophotonics in the past century. Owing to their intriguing features, such as sub-diffraction limit, environment sensitivity, field confinement, and enhancement, the SPs have hosted a wide scope of applications including ultrahigh-sensitivity biosensing,² super-resolution imaging,³ sub-wavelength lithography,⁴ surface-enhanced Raman spectroscopy, etc.

Of great interest is the SP localized on metallic nanoparticles (NPs) (termed as localized surface plasmon (LSP)), which can lead to a significant enhancement of electromagnetic field at the particle surface.⁵ This enhancement is widely accepted as the major contribution in a surface-enhanced Raman spectroscopy,⁶ a powerful analytical tool for chemical and biological sensing applications. The magnitude of enhancement ranges from 10 to 10⁵, depending on the particles size,⁷ shape,⁸ composite, arrangement,^{9,10} and the incident light polarization.¹¹ Single molecule sensitivity has been realized,^{11,12} which requires a Raman enhancement (square of electromagnetic enhancement) at the order of 10¹⁴. Such huge enhancement exists on a NP dimer structure or aggregates and arises from the strong coupling between LSP on each particle.⁹ Recent works demonstrated that the introduction of SPPs, another form of SPs supported at a smooth metal surface or periodic metallic structure, into the conventional LSP-only SERS system could improve further the Raman enhancement^{13,14} by an order of 10–10². Meanwhile, the corresponding SERS substrates possess a much higher reproducibility compared to the aforementioned dimer structure.¹⁵ These attractive properties make them great candidates as robust SERS substrates.

Besides the SPPs contribution on the excitation of SERS signals, recent experimental works demonstrated that the emitted Raman radiation is also able to couple to SPs with periodic metallic structure¹⁶ or nanoantennas,^{17,18} forming a “beam shaped” Raman scattering. Such shaped emission of Raman scattering is able to improve its collection efficiency.

In this work, we investigate the emission pattern of SERS from single NP-film junction. Because of the presence of a thin metal film, Raman scattering from the NP-film junction is able to couple back to SPPs supported at the air-metal interface and eventually re-radiates into the substrate side with higher refractive index. The so-called surface plasmon coupled emission (SPCE)^{19–25} is able to improve the collection efficiency of SERS, and the SPCE curve from SERS can also be used for measuring the propagation length of SPPs and the point spread function (PSF) of an SPCE microscopy.

The schematic diagram of experimental setup is shown in Fig. 1(a). A collimated radially polarized laser beam is employed as the excitation source, which is of great advantages compared to the conventional linearly polarized Gaussian beam because of its donut shape beam profile and its unique property of full-beam *p*-polarization.¹³ It is converted from a circularly polarized beam by using a spiral phase element and a radial-type analyzer.²⁶ A high numerical aperture (NA) oil immersion objective lens (Olympus, 60×, NA = 1.49) is used to tightly focus the incident beam onto the sample to excite SPPs and collect the SPCE of SERS. Raman signals at the transmission direction are collected with an Olympus objective lens. A black&white CCD camera (CCD1) is used at the transmission direction or back image plane to obtain the Raman image of individual nanospheres, while a color one (CCD2) placed at the back fourier plane is used to record the reflected laser beam (without a filter placed before CCD2) or emission pattern of SERS (with a filter placed before CCD2, as shown in Fig. 1(a) with a dashed rectangle), respectively. Raman spectrum originated from the sample is analyzed with a TEC-cooling spectrometer, both at the transmission and reflection directions (CCD2 is replaced with the spectrometer when collecting the Raman spectrum at the reflection direction).

The sample is a sandwiched structure composing of isolated silver nanosphere immobilized on a thin silver film, with 4-mercaptobenzoic acid (4-mba) molecules sandwiched between them (Fig. 1(b)). It is prepared with the following processes: (1) Silver film with thickness ~55 nm is first formed by electron beam deposition onto a cleaned glass

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FIG. 1. (a) Experimental setup investigating the emission pattern of SERS. (b) A detailed view of the sample, which is a sandwiched structure composing of isolated silver nanosphere (60 nm-diameter) immobilized on a thin silver film (55 nm-thickness), with 4-mba molecules sandwiched between them. (c) SERS spectrum of 4-mba molecules emitted from single nanosphere-film junction. Integration time is 5 s. In the text, we are referring to all the Stoke's scattering as marked since all the Raman peaks change in the same proportion with the change of excitation intensity and integration time.

coverslip; (2) the coated substrate is then immersed for around 30 min in a 10^{-3} M ethanolic 4-mba solution to form a self-assembled monolayer of 4-mba molecules, which is subsequently rinsed with ethanol and DI water to remove the excess molecules on the surface; (3) a droplet of diluted silver colloids (diameter ~ 60 nm, $100 \mu\text{l}$, $\sim 10^9$ nanospheres/ml) is applied onto the 4-mba/Ag plane and allowed to evaporate naturally, followed by water-rinsing and air-drying at ambient temperature.

For a three layer system composing of a thin silver film sandwiched by semi-infinite air environment and glass substrate (Fig. 2(a)), the transmission coefficient of electric field for a p -polarized beam can be calculated as following:

$$\tau_p = \frac{t_p^{12} t_p^{23} \exp(ik_2 t \cos \theta_2)}{1 + r_p^{12} r_p^{23} \exp(2ik_2 t \cos \theta_2)}. \quad (1)$$

t_p^{12} and t_p^{23} are the Fresnel transmission coefficients for each of the respective two-layer interfaces and r_p^{12} and r_p^{23} the corresponding reflection coefficients. The two-layer coefficients can be calculated by the following equations:

$$t_p^{ij} = \frac{2n_{ij} \cos \theta_i}{n_{ij}^2 \cos \theta_i + \sqrt{n_{ij}^2 - \sin^2 \theta_i}}, \quad (2)$$

$$r_p^{ij} = \frac{n_{ij}^2 \cos \theta_i - \sqrt{n_{ij}^2 - \sin^2 \theta_i}}{n_{ij}^2 \cos \theta_i + \sqrt{n_{ij}^2 - \sin^2 \theta_i}}, \quad (3)$$

$$n_{ij} \equiv \frac{n_j}{n_i}, \quad i = 1, 2; \quad j = 2, 3, \quad (4)$$

where θ_i ($i=1,2$) are the incident angles at each interface and are linked by the Snell's Law, n_i and k_i are, respectively,

FIG. 2. Transmission features of a three-layer system modelling the proposed excitation configuration of SPPs. (a) Schematic view of the system for the calculation, which includes a 55 nm-thickness silver film sandwiched by semi-infinite air and glass substrate. (b), (c) Calculated transmittance in case of glass-side incidence and air-side incidence, respectively. The sharp transmission peak in (b) demonstrates the excitation of SPPs when incident light illuminates from the glass substrate, while that in (c) illustrates the surface plasmon coupled emission of light from air into the glass substrate, both at SPP excitation angles. (d) Reflected laser beam profile obtained at the back fourier plane of the objective lens (NA = 1.49), with a sharp dark ring representing the excitation of SPPs from all azimuthal directions. (e) Emission pattern of SERS at SPP excitation angles, forming an SPCE ring.

the refractive index and wave-vector at each layer, and t the thickness of metal film.

Consider that incident light is illuminated from the glass side into air, passing through the thin silver film. Under this circumstance, θ_3 is the incident angle while θ_1 the transmitted. The calculated transmittance T ($T = \tau_p^2$) plotting against the incident angle according to Eq. (1) is presented in Fig. 2(b). One can see a sharp transmission peak at incident angle around 44° . This corresponds to the SPP excitation angle, which can be derived with the wave-vector matching condition

$$k_{spp} = k_0 n_3 \sin \theta_3 = k_0 \sqrt{\frac{\epsilon_1 \cdot \epsilon_2}{\epsilon_1 + \epsilon_2}}. \quad (5)$$

The significantly enhanced transmittance near SPP excitation angle results in the well known field enhancement effect of SPPs. Correspondingly, at the back Fourier plane, as incident radiations near the SPP excitation angle are strongly coupled to SPPs at the silver-air interface, a sharp dark ring can clearly be seen at the reflected beam (Fig. 2(d)), due to the full-beam p -polarization of a radially polarized light.

We now consider that incident light is illuminated from air into the glass side (θ_1 is the incident angle, θ_3 the transmitted). The calculated transmittance plotting against the incident and transmitted angle is illustrated in Fig. 2(c). As shown with the inset, the transmittance is very low over the whole range of available incident angles. This is due to the special refractive index of metal, which has a small real part (high reflection) and a large imaginary part (high absorption). Situation is changed if we consider it from the perspective of transmitted angle. A sharp transmission peak is present at the curve, with the corresponding transmitted angle exactly same with the resonant incidence angle in Fig. 2(b). The transmittance at this angle is calculated to be 600%. It is ~ 300 times enhanced compared to that at smaller angles, which is from the available incident angles. Such giant enhancement is thus coming from the evanescent incident radiations at the air side, which have in-plane wave-vector component identical to that of SPPs supported at the silver-air interface and hence are able to couple to SPPs and re-radiates into the glass side at SPP excitation angle.

In our experiment, SPPs are first excited by a tightly focused radially polarized beam. The SPPs subsequently interact with the silver NPs on the silver film, leading to a plasmon-hybridized gap-mode with electric field significantly enhanced at the NP-film junction.¹³ The enhanced electric field is then to excite SERS of 4-mba molecules sitting at the junction (Fig. 1(c)). Due to the scattering nature of SERS, the evanescent radiation component with in-plane wave-vector equal to k_{spp} is able to couple to SPPs and eventually re-radiates into the glass side at SPP excitation angle, forming an SPCE ring at the back fourier plane (Fig. 2(e)).

Attention now paid on the role of SPPs played in our gap mode SERS system, which is analogue to the one LSP played in a conventional SERS system. In a conventional system, the power of enhanced Raman radiation can be calculated as¹

$$P \propto N\sigma_{\text{SERS}} \cdot \frac{|E_{\text{loc}}|^4}{|E_0|^4} \cdot |E_0|^2, \quad (6)$$

where N is the number of Stokes-active scatters within the hotspot, σ_{SERS} the scattering cross section, and E_{loc} and E_0 the amplitudes of the enhanced and incident electric field, respectively. The contribution from LSP is illustrated with the fourth-order factor, which is due to the enhancement of both the incident and emitted light field.

Similarly, in our system, incident light is first enhanced by the excitation of SPPs at the silver-air interface, as illustrated with Fig. 2(b). The emitted Raman radiation is finally enhanced through the SPCE, as shown in Fig. 2(c). The only difference arises from their different excitation schemes. LSP can be excited with light of appropriate frequency and polarization, irrespective of its wave-vector. As a result, the enhancement factor for the incoming and emitted light field is very close and hence can be consolidated, leading to a fourth-order effect. The excitation condition for an SPP, however, is strongly wave-vector dependent, which is demonstrated with the wave-vector matching condition (Eq. (5)). The additional condition results in an excitation of SPPs with incident light and an emission of the emitted Raman

scattering at fixed angles (i.e., SPP excitation angles) based on the attenuated total reflection configuration.

Thus, the total power of Raman radiation collected can be expressed as

$$P \propto N\sigma_{\text{SERS}} \cdot \frac{|E_{\text{loc}}|^4}{|E_{\text{SPP}}|^4} \cdot |E_{\text{SPP}}|^2 \cdot \text{CE}(\text{SPCE}). \quad (7)$$

The fourth-order factor illustrates the enhancement induced by the plasmon-hybridized gap mode, while the last two terms represent the enhancement from SPPs, in terms of the SPPs excitation with incident light and collection efficiency (CE) improvement through SPCE, respectively.

To illustrate the collection efficiency improvement through the SPCE, we now compare the intensity of Raman signal collected at the glass side (SPCE) to that collected at the air side (conventional), with the result shown in Fig. 3. In the experiment, rhodamine 6G molecule was used as the Raman probe, instead of the 4-mba molecule used previously and thereafter. The improvement of collection efficiency can clearly be seen in Fig. 3. The Raman intensity ratio (SPCE/conventional) is fluctuating between 3 and 5 as we move the stage, which is mainly because of the non-uniform distribution of NPs immobilized on the metal film. Although the collection efficiency at the air side can further be magnified by using a higher NA objective lens, the bottom line here is that Raman signal collected via SPCE is comparable to that collected directly in the air.

While such improvement does not seem notable for a SERS system, it is of great significance for a tip-enhanced Raman spectroscopy (TERS),²⁷ in which Raman signal is either side-collected with a long working distance objective lens (reflection mode) or collected at the opposite side to the metallic tip with respect to the substrate (transmission mode). The collection efficiency under both configurations is very low. This, however, can be significantly improved by introducing a thin metal film as the substrate, and hence SPCE occurs in the system. In addition, the SPP excitation with incident light can also greatly improve the excitation efficiency because of its field enhancement, as demonstrated in Eq. (7).

FIG. 3. Intensity comparison between the Raman signals of R6G molecules collected at the glass side through SPCE and collected directly at the air side (conventional). Integration time is 1s. Collection efficiency is shown to be enhanced through SPCE.

The SPCE of SERS can further be verified with the real-space image of single nanosphere captured at the back-image plane, as shown in Fig. 4(a). A donut shape encircled by a set of concentric rings can clearly be seen, which agrees well with the calculated PSF of an SPCE microscopy (Fig. 4(b)) obtained according to the formulas derived in Ref. 22. This is due to the small excitation area of Raman scattering within the NP-film junction, which is far below the size restricted by the optical diffraction limit, and hence can be treated as a point source. In addition, because of the sharper linewidth of Raman spectrum, the gap mode SERS can approximately serve as a point source possessing multiple single-wavelengths for the excitation of SPP and hence the PSF obtained with SERS is much close to the theoretical one compared to that obtained with fluorescence.²⁴

The single-wavelength nature of Raman spectrum can also lead to an accurate measurement of the propagation length of SPPs. More specifically, the transmission curve of an SPCE ring (Fig. 2(e)) can approximately be described as a Lorentz curve, of which the full-width at half-maximum (FWHM) encodes the propagation length of an SPP ($1/\text{FWHM}$).^{25,28} In our work, the Lorentz function of

$$I = I_0 + \frac{2A}{\pi} \frac{\omega}{4(k - k_0)^2 + \omega^2} \quad (8)$$

is used to fit the SPCE ring, where ω represents the FWHM of the fitted curve and is equal to $0.09931 \mu\text{m}^{-1}$. The propagation length of the excited SPPs is hence $1/\omega$, which equals to $10.069 \mu\text{m}$. This agrees well with the theoretical one ($9.16 \mu\text{m}$) derived from the calculated transmittance curve. The measurement error is believed from the limited CCD pixels near SPP excitation angle and the background noises. Fluorescence spectrum, on the contrary, has a wide

FIG. 4. Raman image of individual nanosphere captured at the back image plane of the objective lens ($\text{NA} = 1.49$) through SPCE, which is approximately the pattern of point spread function of an SPCE microscopy because of the small excitation area of SERS within the nanosphere-film junction. (a) Experimental, (b) calculated, and (c) their cross-section comparison across the center. The experimental result accords well with the theoretical one.

linewidth. As a result, the obtained SPCE ring from fluorescence is typically much broader than the one from SERS, and the measured SP propagation length is therefore underestimated.

To sum up, the SPCE of SERS from NP-film junction was investigated in this work. Because of the presence of a thin silver film, Raman scattering is able to couple to SPPs and emits into the substrate side with higher refractive index. Transmission coefficient is shown to be greatly enhanced at the SPP excitation angle. As a result, the SPCE can serve as a high sensitivity detection tool for SERS and particularly for TERS. Meanwhile, due to the extremely sharp linewidth of Raman peaks, SERS can be employed as a multiple single wavelength sources for the excitation of SPPs and is well-suited for the measurement of propagation length of SPPs and quantitative characterization of the PSF of an SPCE microscopy.

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- ¹S. Maier, *Plasmonics: Fundamentals and Applications* (Springer, New York, 2007).
- ²J. Homola, S. S. Yee, and G. Gauglitz, *Sens. Actuators, B* **54**, 3 (1999).
- ³J. B. Pendry, *Phys. Rev. Lett.* **85**, 3966 (2000).
- ⁴N. Fang, H. Lee, C. Sun, and X. Zhang, *Science* **308**, 534 (2005).
- ⁵K. A. Willets and R. P. Van Duyne, *Annu. Rev. Phys. Chem.* **58**, 267 (2007).
- ⁶P. L. Stiles, J. A. Dieringer, N. C. Shah, and R. R. Van Duyne, *Annu. Rev. Anal. Chem.* **1**, 601 (2008).
- ⁷K. L. Kelly, E. Coronado, L. L. Zhao, and G. C. Schatz, *J. Phys. Chem. B* **107**, 668 (2003).
- ⁸J. J. Mock, M. Barbic, D. R. Smith, D. A. Schultz, and S. Schultz, *J. Chem. Phys.* **116**, 6755 (2002).
- ⁹E. Hao and G. C. Schatz, *J. Chem. Phys.* **120**, 357 (2004).
- ¹⁰D. W. Brandl, N. A. Mirin, and P. Nordlander, *J. Phys. Chem. B* **110**, 12302 (2006).
- ¹¹S. M. Nie and S. R. Emery, *Science* **275**, 1102 (1997).
- ¹²K. Kneipp, Y. Wang, H. Kneipp, L. T. Perelman, I. Itzkan, R. Dasari, and M. S. Feld, *Phys. Rev. Lett.* **78**, 1667 (1997).
- ¹³L. P. Du, G. H. Yuan, D. Y. Tang, and X. C. Yuan, *Plasmonics* **6**, 651 (2011).
- ¹⁴L. P. Du, X. J. Zhang, T. Mei, and X. C. Yuan, *Opt. Express* **18**, 1959 (2010).
- ¹⁵W. H. Park, S. H. Ahn, and Z. H. Kim, *ChemPhysChem* **9**, 2491 (2008).
- ¹⁶Y. Z. Chu, W. Q. Zhu, D. X. Wang, and K. B. Crozier, *Opt. Express* **19**, 20054 (2011).
- ¹⁷A. Ahmed and R. Gordon, *Nano Lett.* **11**, 1800 (2011).
- ¹⁸W. Q. Zhu, D. X. Wang, and K. B. Crozier, *Nano Lett.* **12**, 6235 (2012).
- ¹⁹N. Calander, *Anal. Chem.* **76**, 2168 (2004).
- ²⁰I. Gryczynski, J. Malicka, Z. Gryczynski, and J. R. Lakowicz, *J. Phys. Chem. B* **108**, 12568 (2004).
- ²¹I. Gryczynski, J. Malicka, K. Nowaczyk, Z. Gryczynski, and J. R. Lakowicz, *J. Phys. Chem. B* **108**, 12073 (2004).
- ²²J. R. Lakowicz, *Anal. Biochem.* **324**, 153 (2004).
- ²³J. Enderlein and T. Ruckstuhl, *Opt. Express* **13**, 8855 (2005).
- ²⁴W. T. Tang, E. Chung, Y. H. Kim, P. T. C. So, and C. J. R. Sheppard, *Opt. Express* **15**, 4634 (2007).
- ²⁵D. G. Zhang, Q. Fu, M. F. Yi, X. X. Wang, Y. K. Chen, P. Wang, Y. H. Lu, P. J. Yao, and H. Ming, *Plasmonics* **7**, 309 (2012).
- ²⁶K. J. Moh, X. C. Yuan, J. Bu, R. E. Burge, and B. Z. Gao, *Appl. Opt.* **46**, 7544 (2007).
- ²⁷N. Hayazawa, Y. Saito, and S. Kawata, *Appl. Phys. Lett.* **85**, 6239 (2004).
- ²⁸N. Hartmann, G. Piredda, J. Berthelot, G. C. D. Francs, A. Bouhelier, and A. Hartschuh, *Nano Lett.* **12**, 177 (2012).