Surface Raman spectroscopy with and without reverse Kretschmann configuration: Effect of evanescent-wave-coupled emission

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Received April 12, 2016; accepted April 19, 2016; published online May 18, 2016

Evanescent-wave-coupled emission has been used for reverse Kretschmann fluorescence and Raman spectroscopies with high collection efficiency. However, it has a negative effect on the common surface-enhanced Raman spectroscopy and tip-enhanced Raman spectroscopy without the reverse Kretschmann configuration because the coupling of a large fraction of light power into the substrate impairs the Raman signal backscattered in air. A rough core layer can significantly weaken evanescent-wave-coupled emission, which is conducive to enhancing the backscattered Raman signal. In this work, we theoretically investigate the surface-plasmon-coupled emission and its effects on surface Raman spectroscopy. © 2016 The Japan Society of Applied Physics

Urfaced-enhanced Raman spectroscopy (SERS) generally detects backscattered light, and it utilizes the localized surface plasmon resonance (LSPR) of metallic nanostructures to achieve high sensitivity.1–10 Raman light backscattered from conventional SERS substrates is highly divergent, resulting in low collection efficiency. The reverse Kretschmann (RK) Raman spectroscopy is a new technique relative to SERS, which is based on evanescent-wave-coupled emission (EWCE), including surface-plasmon-coupled emission (SPCE) and waveguide-mode-coupled emission (WMCE). The RK Raman spectroscopy allows for high-efficiency signal collection.11–16

EWCE is a directional emission in the substrate of photons radiated from molecular dipoles located within the penetration depth of an evanescent field, which is based on the local field interaction with the photons. It does not involve the photon-producing process in the vicinity of the surface.10 The excitation source used for EWCE is either a free-space laser beam or an evanescent wave generated under the surface plasmon resonance (SPR) or waveguide mode resonance (WMR) condition. As long as the core layer satisfies the SPR or WMR condition, EWCE will inevitably occur for radiation from the surface of the core. The radiation from the surface of the core can be Raman, fluorescence, or elastic scattering. The EWCE-based directional emission, however, can be observed only in the presence of the RK configuration. This technique is called RK fluorescence or Raman spectroscopy. In the absence of the RK configuration, the light launched in the substrate by EWCE cannot become directional radiation in free space. This part of light power will be dissipated by SPR absorption or surface scattering. This means that EWCE has a negative effect on the backscattered Raman detection methods, including conventional SERS and tip-enhanced Raman spectroscopy (TERS). This issue, however, has not yet been paid any attention so far.

Since SPCE is more attractive and more useful than WMCE, the SPCE effect with gold or silver films was theoretically analyzed in this work, which is based on the optical reciprocity theorem. The optical reciprocity theorem can be briefly described as follows:17 the power density \( P(r) \) propagating in the direction \( r \) of light from a molecular dipole located in a layered structure is proportional to the square of the field enhancement factor \( (\text{EF}_{\text{field}}) \) induced at the dipole position by the plane wave of the same wavelength propagating in the direction opposite to \( r \). By setting the square of the amplitude of the dipole as \( p^2 = (12\pi\varepsilon_0 c^2/\omega^4)W \) for normalizing the total radiation power of the dipole in free space,17 \( P(r) \) at a distance (\( r = 1 \) m) can be expressed as

\[
P(r) = \frac{3n_p}{8\pi} \text{EF}_{\text{field}}^2 e_r [\text{W/m}^2],
\]

where \( n_p \) is the RI of the medium in which light propagates, and \( \text{EF}_{\text{field}} \) with a multilayer structure can be precisely calculated using the Fresnel theory.18,19 Note that in Eq. (1), only SPCE is taken into consideration and no excitation source is involved. When the excitation source is an SPR wave, \( P(r) \) is approximately proportional to the fourth power of \( \text{EF}_{\text{field}} \) (\( \text{EF}_{\text{field}} \) with the SPR wave is somewhat different from \( \text{EF}_{\text{field}} \) owing to different wavelengths).

Figure 1 schematically shows the RK Raman spectroscopy setup with the excitation source being the SPR wave or a free-space laser beam. According to Ref. 13, the excitation wavelength is 647 nm, the silver film is 50 nm thick, and its RI is 0.1399 + i4.3157. The glass substrate and the glass prism have the same RI of 1.5145, and they were in close contact with each other via the RI-matched liquid. A monolayer of Nile blue molecules was adsorbed on the silver film for Raman emission. SPR was first excited at an incident angle of \( \theta = 42.9^\circ \) for evanescent wave excitation of the Raman signal. The typical Raman fingerprint of \( \Delta \nu = 590 \text{ cm}^{-1} \) for Nile blue was observed by RK Raman spectroscopy. \( \Delta \nu = 590 \text{ cm}^{-1} \) corresponds to the emission wavelength of \( \lambda = 672.7 \text{ nm} \). This wavelength was used in all calculated results below. Since SPR is not sensitive to the adsorption of small molecules, the Nile blue monolayer was neglected in the calculation process.

Figure 2 shows the radiation patterns in the \( xz \)-plane for the photons emitted from the molecular dipoles located on the silver film with different orientations. It is evident that the radiation in the prism side has a well-defined direction and that in the air side lacks directionality. The directional radiation in the prism is the so-called SPCE signal, which arises from the coupling of the photons into the SPR wave.
accompanied by the recoupling of the SPR wave into the directional light in the prism. The SPCE signal in Fig. 2(a) is associated with the \( z \)-component \( (E_z) \) of the electric field of the SPR wave and that in Fig. 2(b) is associated with \( E_x \). Since \( E_z \) is stronger than \( E_x \), the SPCE intensity in Fig. 2(a) is higher than that in Fig. 2(b). Figures 2(a) and 2(b) also indicate that the presence of SPCE significantly impairs the backscattered light in the air side. This suggests that SPCE plays a negative role in the common backscattered Raman detection. The SPR wave is TM polarized, and this feature leads to the absence of SPCE in Fig. 2(c), consequently making the backscattered signal in the air side very strong.

To determine the power fraction occupied by the SPCE signal in the prism, the radiation patterns in the \( xz \)-plane for the emission from the molecular dipole of different orientations on the silver film were calculated. Figures 3(a)–3(d) show the calculated results. With the \( z \)-oriented dipole, the radiation pattern in the prism side is a closed circle [Fig. 3(a)], on which the SPCE power is uniformly distributed. From the three-dimensional perspective, the SPCE signal in the prism forms a light cone referred to as the Kretschmann cone, and the half-angle of the cone (namely, the SPCE angle) is equal to the SPR resonance angle. The closed circle in Fig. 3(a) is the cross section on the \( xy \)-plane of the Kretschmann cone. The radiation pattern in the air side is a disc comprising multiple closed circles of different radii [Fig. 3(b)]. Different circles represent different power densities. There is no power density at the center of the disc. It was derived from Figs. 3(a) and 3(b) that the fraction of the SPCE power in the prism side is 58.48% and the backscattered radiation in the air side occupies 41.52% of the total emission power. Figure 3(c) shows the radiation pattern in the prism side with the \( y \)-oriented dipole. The pattern is an open circle with two openings in the \( x \)-direction. The power density at each opening is almost zero, suggesting a lack of SPCE signal. This is in agreement with Fig. 2(c). The radiation pattern in the air side with the \( y \)-oriented dipole [Fig. 3(d)] is quite different from that with the \( z \)-oriented dipole. It contains multiple runway-type ellipses representing the equal-power-density profiles. With Figs. 3(c) and 3(d), it was determined that the power fraction of the SPCE signal is 31.26% with the \( y \)-oriented dipole, which is smaller than that with the \( z \)-oriented dipole. Assuming that the molecular dipoles are disorderly arranged on the silver film, the average power fraction of the SPCE signal in the prism side is 44.87% and that of the backscattered signal in the air side is 55.13%. Note that the power distribution between the SPCE signal in the prism and the backscattered signal in air is dependent on the thickness of the silver film. Although the SPCE power is lower than the backscattered signal power with a 50-nm-thick silver film, the SPCE signal allows for high-efficiency collection using the RK Raman spectroscopy technique because of its excellent directionality. On the other hand, a combination of Figs. 2 and 3 reveals that the prism is indispensable for the effective detection of the SPCE signal but dispensable for SPCE generation. In other words, SPCE can take place in the conventional SERS measurements as long as the SERS substrates used contain gold or silver films.
In this case, SPCE plays a negative role in the measurement because the conventional SERS technique detects the backscattered Raman light. In the absence of the RK configuration, the SPCE signal in the metal-coated substrate cannot become directional radiation in free space. This part of light power will be dissipated by SPR absorption, which would significantly reduce the sensitivities of SERS and TERS techniques because they detect backscattered Raman light in air. Figure 4 schematically shows the TERS setup. TERS is usually performed by the deposition of a monolayer of target molecules on an atomically flat gold surface. In the TERS measurement, Raman photons can be strongly coupled to the SPR wave at the gold/monolayer interface, leading to a significant reduction in the number of backscattered Raman photons available for detection.

To verify the SPCE-induced Raman extinction, the radiation patterns in the xz-plane for TERS were simulated by the FDTD method (Lumerical Solutions FDTD solutions 8.6). The calculation parameters are as follows: the radiation wavelength is 532 nm, the metal tip is equivalent to a gold nanosphere of 50 nm diameter, and the air gap between the metal tip and the surface of the gold film is 3 nm. The RI of the glass substrate is 1.52 at 532 nm wavelength. Figure 5(a) shows the simulation model with a 50-nm-thick gold film and the corresponding radiation pattern. The strong SPCE signal exists in the glass substrate, but it cannot become directional emission in free space owing to the absence of the prism coupler. This SPCE signal will be scattered in air from the lateral surface of the glass substrate or absorbed by the gold layer. Owing to the presence of the SPCE signal in the substrate, the backscattered Raman signal in air is quite weak. Figure 5(b) shows the calculated result with a 500-nm-thick gold film. No SPCE signal occurs in the glass substrate, and the backscattered Raman signal in air is almost as weak as that in Fig. 5(a). A comparison between Figs. 5(a) and 5(b) reveals that the strong coupling of Raman photons to the SPR wave can take place with the two gold films of 50 and 500 nm thicknesses. However, the 50-nm-thick gold film allows the SPR wave to be recoupled into the glass substrate to generate the SPCE signal, but the 500-nm-thick gold layer does not enable the SPR recoupling to effectively take place. This is because the evanescent field of the SPR wave cannot penetrate the 500-nm-thick gold layer to interact with the lower glass substrate. As a result, the SPR wave is absorbed by the gold layer.

Therefore, although the SPCE signal disappears in the glass substrate with a 500-nm-thick gold layer, the backscattered Raman signal cannot be effectively enhanced. Even with a bulk gold crystal having an atomically flat surface for TERS application, the strong coupling of Raman photons to the SPR wave can still spontaneously take place because such a gold surface satisfies the SPR condition. The spontaneous coupling of Raman photons to the SPR wave inevitably weakens the backscattered Raman signal, consequently reducing the detection sensitivity of SERS and TERS techniques. As a matter of fact, as long as the evanescent wave at a Raman wavelength can be generated on the surface of a substrate, the corresponding Raman photons emitted from the surface can be launched into the substrate through the EWCE mechanism, leading to a reduction in the intensity of the backscattered Raman signal. For example, when a slide glass substrate coated with a monolayer of gold nanoparticles is used for SERS measurement, a large number of Raman photons can be coupled into the substrate through their interaction with the strong evanescent field generated via total reflection at an angle close to the critical value. As a result, the number of Raman photons backscattered in air will be decreased.

The above-mentioned analyses can be used to explain the abnormal experimental results reported in the literature. One example is nanoporous-gold (NPG)-based SERS substrates. NPG-based SERS substrates have been widely studied because of their large surface-to-volume ratio and salient LSPR effect. It was found in practical applications that the SERS enhancement factor with conventional NPG films is rather low.\textsuperscript{19,20} The reason behind this fatal flaw of NPG-based SERS substrates remained unknown until now. Taking into account the fact that the NPG film allows us to excite the SPR wave on its surface,\textsuperscript{21} the spontaneous coupling of Raman photons to the SPR mode is inevitable, which would weaken the backscattered Raman signal. This may be the reason for the low SERS sensitivity observed with the NPG film. One way to minimize the negative effect of the coupling of Raman photons to the SPR mode is to increase the surface roughness of substrates. According to the Fresnel theory, the larger the surface roughness, the smaller the field en-

![Fig. 4. SPCE-induced extinction of TERS signal (the TERS signal generated in the near-field region is coupled to SPR waves and is finally eliminated by the gold film, making the collected signal weak).](image1)

![Fig. 5. FDTD simulation results of intensity ($E^2$) patterns from the molecular dipole located between the gold nanosphere and the gold film (a) with 50-nm-thick gold film; (b) with 500-nm-thick gold film).](image2)
hancement factor (EFfield). From Eq. (1), a small EFfield can effectively suppress the coupling of Raman photons into the SPR mode, consequently increasing the number of backscattered Raman photons. To understand the effect of surface roughness on the field enhancement factor of the SPR mode (here, the surface-roughness-induced LSPR effect is not considered because it is beyond the scope of this work), a four-layer structure consisting of a glass prism (1.785 at \( \lambda = 785 \) nm), a 50-nm-thick gold layer (0.178 + i4.971), a 10-nm-thick SiO2 layer (1.46), and air cladding is used as the simulation model. In the calculation process, the surface roughness is taken into consideration by introducing an imaginary part (k) of RI to the SiO2 layer (a larger surface roughness corresponds to a larger imaginary part of RI). Figure 6(a) shows the angle distributions of the local EFfield calculated with different imaginary parts of RI. The EFfield reaches the maximum at the SPR resonance angle. Figure 6(b) shows a plot of the maximum EFfield against the imaginary part of RI. As expected, the maximum EFfield decreases with increasing imaginary part of RI. The simulation results combined with Eq. (1) indicate that a rough surface of the metallic substrates enables the reduction of the EFfield, thereby weakening the coupling of Raman photons to the SPR mode. Weakening the coupling of Raman photons to the SPR mode would intensify the backscattered Raman signal. In addition to repressing EFfield, a large surface roughness is conducive to the conversion of the SPR wave into the scattered light in air and consequently to the enhancement of the SERS sensitivity. This SERS enhancement mechanism is different from the well-recognized electromagnetic and chemical enhancements. The reported studies have demonstrated that the wrinkling and nanopatterning of NPG films can significantly increase the SERS enhancement factor.22,23 It is worth noting that the above inferences are also applicable to the waveguide-based Raman spectroscopy.

In summary, the unique characteristics of SPCE and its effects on both the RK Raman spectroscopy and the SERS/TERS techniques were analyzed on the basis of a combination of the optical reciprocity theorem and the Fresnel reflection formula. SPCE arises from the spontaneous coupling of photons emitted from surface-bound molecular dipoles into the SPR wave and the recoupling of the SPR wave into the directional radiation in the dielectric substrate. This mechanism indicates the two conditions for the occurrence of SPCE. One condition is to position molecular dipoles in the penetration depth of the evanescent field, and the other condition is to control the thickness of the metal film to enable the evanescent field to penetrate it. In the presence of the prism coupler, the SPCE signal can be coupled into air to be detected by RK Raman spectroscopy. In the absence of the prism coupler, the SPCE signal cannot be detected and it will dissipate in the substrate. SPCE plays a negative role in the SERS and TERS techniques because SPCE induces a significant reduction in the number of backscattered Raman photons. More strictly speaking, it is the spontaneous coupling of photons emitted from surface-bound molecular dipoles into the SPR wave that can reduce the sensitivities of SERS and TERS techniques. This negative effect can be mitigated by increasing the surface roughness of substrates. A large surface roughness can suppress the coupling of Raman photons into the SPR wave and is also conducive for converting the SPR wave into scattered light in air, which is collected together with the originally backscattered Raman photons. In this work, we introduced a new way of understanding the SPCE, SERS, and TERS effects and their relationships, and it is also considered to be helpful for enhancing the sensitivities of SPCE, SERS, and TERS techniques.

Acknowledgments This work was supported by the National Key Basic Research Program of China (No. 2015CB352100), the National Natural Science Foundation of China (No. 61377064), the Major National Instrument and Equipment Development Project of China (No. 2011YQ0301240802), the Research Equipment Development Project of the Chinese Academy of Sciences (No. YZ201508), and the State Key Laboratory of NBC Protection for Civilian, China (SKLNBC2014-11).

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