Research article

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Directional surface plasmon-coupled emission of tilted-tip enhanced spectroscopy

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Abstract: Understanding the spatial radiation pattern in tip-enhanced spectroscopy (TES) is crucial for plasmon-enhanced spectroscopy, chemical analysis and biochemical sensing. Although the TES technique has many excellent advantages, there is still room for improvement in terms of detection sensitivity. In this paper, we theoretically demonstrate the tip-tilted TES configuration featuring high directivity by using side illumination-collection condition. Taking full advantage of the characteristic of high directional emission ascribed to the far-field interference between localized surface plasmon resonance (LSPR) and surface plasmon polariton (SPP) modes, the collection efficiency of TES signals can be largely improved, greatly boosting the detection sensitivity of TES technology. Our theoretical results not only provide a deep understanding of the underlying physical mechanism of the directional surface plasmon-coupled emission of TES, but also serves as a promising guide for the rational construction of a highly efficient TES platform at the single molecular level.

Keywords: surface plasmon-coupled emission; tip-enhanced spectroscopy; surface plasmon resonance; detection sensitivity.

1 Introduction

Single molecule detection is still one of the key goals of most interface-enhanced spectroscopy studies [1–6].

Utilizing surface plasmon resonance (SPR) to improve the enhancement factor is a direct way to increase the detection sensitivity. However, a Raman enhancement factor up to 10^{10} is required to meet the demands of the single molecule detection of probe samples with low scattering cross section [7]. Generally, the experimental substrates hardly provide sufficiently high enhancement factors. Furthermore, the intense local electromagnetic field always inevitably destroys portions of target molecules in most cases. Therefore, seeking other feasible methods to improve the detection sensitivity is a very urgent task in single molecule studies.

Experiments demonstrated that improving the collection efficiency of molecular signals can greatly boost the detection sensitivity of the spectrum instruments [8–11]. In free space, the molecular scattering is isotropic and only 1% signal can be collected by conventional detection method [12]. However, the low collection efficiency is easily ignored in many past experiments on plasmon-enhanced spectroscopies. Due to the novel property of highly directional emission, the rapidly developed surface plasmon-coupled emission (SPCE) technique offers a new way of signal detection with high collection efficiency [13–17], thereby effectively enhancing the detection sensitivity as high as 1000-fold [18]. Generally, Kretschmann (KR)- and reverse Kretschmann (RK)-based SPCE are elegant methods for improving the collection efficiency of molecular signal [19, 20]. However, the introduction of optical prism makes the experimental facility more complex with large space occupation, thus increasing the experimental costs. Actually, the minimum number of optical components is essential to the integrated and miniaturized spectrometer, such as the tip-enhanced spectroscopy (TES) instruments.

The TES provides a very promising orientation for single molecule studies due to its strong fluorescence enhancement of as high as 1000-fold, Raman enhancement of up to nine orders of magnitudes [21, 22] and high spatial resolution at the sub-nanometer level [23–26]. The three main types of TES configurations based on the illumination-collection method have been used in most laboratories [27]. The bottom illumination-collection

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based TES technique shows high collection efficiency but is limited to producing transparent samples [28]. Meanwhile, the side illumination-collection TES well breaks the sample restriction but suffers from low collection efficiency [29]. The appearance of the top illumination-collection method successfully conquers those problems in the first two TES techniques [30]. In this top illumination-collection TES, a tilted tip is located on top of a substrate while vertically placed tips are used in the bottom and side illumination-collection techniques. Although the top illumination-collection TES combines the advantages of the first two TES techniques with high collection efficiency and unlimited sample, the tip always blocks part of the incident light and molecule scattering signal. In this regard, the tip-tilted side illumination-collection TES configuration is a better choice as it combines the advantages of the side and the top illumination-collection techniques [1]. This new TES configuration shows high directional scattering property, which shall be discussed in subsequent sections.

Both the TES and SPCE can effectively increase the detection sensitivity, where the former utilizes the SPR effect of the tip and the latter concentrates the emission directivity. The combination of TES and SPCE techniques would offer a novel experimental method to develop single molecule detection method by the directionality of SPCE. In relation to this, it is important to carry out theoretical work to study the spatial radiation properties of TES and its underlying physical mechanism, which is important in designing a TES platform with high sensitivity.

In this paper, we demonstrate that high directionality can be realized in a tip-tilted TES configuration. All calculations were performed by using the three-dimensional finite-difference time-domain (3D-FDTD) method. The calculated directional emission patterns show strong dependence on the tip, molecule and the near-field coupling between the tip and film. We believe the calculations

can be good references for the rational construction of TES platform with high sensitivity.

2 Methods

To study in detail the far-field scattering spatial distribution of TES, the 3D-FDTD method was performed, where a conical silver tip over a silver substrate was employed. In accordance with the Near-Field to Far-Field (NTFF) transformation method, the directional emission distributions were obtained based on the calculated near-field data at the transformation surface, which is above the tip and parallel to the substrate. The simulation configuration is depicted in Figure 1. The cone angle, tip-substrate distance and tilt angle of tip are set as β , d and α , respectively. The nanocavity formed by the tip and substrate is illuminated with a p-polarized plane light, where the incident angle, excitation wavelength and electric field amplitude were set as 60° , 532 nm and 1.0 V/m, respectively. In all calculations, the simulation region was set at $1000 \times 1000 \times 1000 \text{ nm}^3$ in 3D, large enough to avoid the disturbance of simulation boundary reflection. We used perfectly matched layer (PML) boundary conditions on all boundaries. To accurately simulate the nanogap between the tip and the substrate, additional non-uniform mesh with size of $0.25 \times 0.25 \times 0.25 \text{ nm}^3$ was used. The optical constant for silver was taken from the experimental report [31].

Figure 1A shows the schematic diagram of the tip-tilted side illumination-collection TES configuration. The colour image shows highly directional TES radiation. By the emission directivity of SPCE, the collection efficiency of TES signal can be largely increased, thus greatly improving the detection sensitivity in real TES experiments. Figure 1B shows the geometric angles under the spherical

Figure 1: Calculation model.

(A) The schematic of the tip-tilted side illumination-collection TES configuration. (B) The geometric angles under the spherical coordinate. The color image shows the highly directional TES radiation.

coordinate, where α , θ and φ are the tilt angle of the tip, the polar angle and the azimuthal angle, respectively.

3 Results and discussion

In order to demonstrate the advantages of the tip-tilted side illumination-collection TES configuration, it is essential to theoretically study the spatial scattering properties of TES with a tilted ($\alpha=15^\circ$) and upright tip ($\alpha=0^\circ$). Figure 2 shows the calculated far-field scattering intensity at the xz -plane ($\varphi=180^\circ$) as a function of polar angle θ . The radius and cone angle of the tip, tip-substrate distance and molecular dipole orientation are $R=20$ nm, $\beta=20^\circ$, $d=1$ nm and $\gamma=90^\circ$, respectively. As shown in Figure 2B, for the vertically placed tip, two main lobe emissions are observed at $\theta=26^\circ$ and -26° due to symmetry. The axisymmetric emission pattern is similar to that observed in a previous study on an Au sphere-film system [19]. Once using a tilted tip, we observe that the vast majority of TES signals concentrate in an emission direction at an angle of $\theta=-26^\circ$, which

presents the single beam pattern. Furthermore, the maximum far-field intensity for the tilted tip is 7.1×10^{-9} , which is 1.2 times higher than the intensity for the vertical tip. Actually, for the vertical tip system, the emission signal is easy blocked by the cantilever of the TES tip, whereas for the tip-tilted side illumination-collection configuration, the TES signal can be greatly collected at the emission orientation, thereby largely boosting the TES sensitivity. We also observed that almost all TES signal radiates into the air side due to the absorption of scattered photons by the thick metal substrate. It should be noted that the results of an optimized plane of $\varphi=180^\circ$ are provided. In our calculations, we found that the maximum far-field intensity decreases gradually, whereas the detection plane changed from $\varphi=180^\circ$ to $\varphi=90^\circ$. Meanwhile, the emission directivity remains unchanged. Hence, the dependence of the far-field intensity on the emission angle θ was just given at the special optimal angle of $\varphi=180^\circ$.

Compared with the vertically placed tip, the tip-tilted TES presents high directivity, which can greatly improve TES detection sensitivity. However, the underlying physical mechanism of the SPCE of TES is still not quite clear.

Figure 2: Calculated far-field intensities for the vertically and obliquely placed tips.

The angle-resolved emission patterns of the TES in the xz -plane obtained for (A) and (B) a dipole emitter with a vertically placed Ag tip of $\alpha=0^\circ$, (C) and (D) a dipole emitter with a obliquely placed Ag tip of $\alpha=15^\circ$. The red arrow in (A) or (C) indicates the vibration orientation of the dipole emitter. The intensities from the film side in (B) and (D) are enlarged 10 times.

It is essential to provide a physical image to deeply clarify the mechanism. Figure 3A shows the synergistic effect of the LSPR and SPP for the SPCE of TES. As the incident radiation illuminates the tip-tilted TES system, the probe molecules and local surface plasmon resonance (LSPR) are excited simultaneously in the nanogap between the tip and the substrate. The excited molecules and the LSPR subsequently arouse the surface plasmon polaritons (SPPs) on the surface of the silver film. Then, the SPPs of the film cooperate with the LSPR of the silver tip, thereby creating the plasmon-hybridized gap-mode that can greatly boost the TES signal of molecules. Two channels exist for the TES signal of molecules. On the one hand, the scattered photons meeting the wave vector matching condition couple to the SPPs and finally decouple into the air showing two main lobe emissions at $\theta = 25.6^\circ$ and -25.6° (due to symmetry), respectively [20], as shown in Figure 3B. On the other hand, most scattered photons are directly scattered by the tip and enhanced by the LSPR [32], presenting a strong emission at $\theta = -26^\circ$ and a weaker emission at $\theta = 23^\circ$ (see Figure 3B). The constructive and destructive interference of the scattered photons from the two channels leads to the high directional scattering pattern of the tip-tilted TES configuration at $\theta = -26^\circ$ in the far field (see Figure 3B). Figure 3C–E show the far-field scattering ($|E|^2$) spatial distributions for the film, tip and tip-film configurations,

respectively. Due to the coherent superposition of the SPP and LSPR modes, we observe high directional TES scattering, as shown in Figure 3E. From Figure 3B, we also observe the emission pattern of the tip-film configuration showing a smaller divergence angle ($\sim 24.5^\circ$) than that of the tip only ($\sim 38^\circ$). This finding implies that the scattering signal becomes more concentrated with the help of the SPP, which is of importance to improve the collection efficiency. The far-field scattering intensity of the tip-film configuration is larger than that of the tip only demonstrating that the SPP could, to some extent, contribute to the increase of the signal intensity (Figure 3D and E).

According to the results of Figures 2 and 3, it seems that a classic top illumination setup with a numerical aperture of 0.9 can capture the entire scattering signal. However, depending on the position and size, the tip blocks a certain amount of excitation light and the scattering signal in the top illumination setup. Hence, especially for tips with a small tilt angle, the side illumination-collection setup would be a better choice. More importantly, during the excitation, the vertical electric field component of the incident light can largely improve the plasmon coupling between the tip and film in the side illumination setup.

In the abovementioned results, the tilted tip plays a dominant role in the TES. Indeed, tilted tips are frequently used in many TES experiments, especially for the top

Figure 3: Physical mechanism of LSPR and SPP contributing to the SPCE of TES.

(A) The schematic of the synergistic effect of the LSPR and SPP for the SPCE of TES. (B) The angle-resolved emission patterns of the TES in the xz-plane obtained for the single tip, film and tip-film configurations, respectively. All intensities are normalized. (C)–(E) The corresponding far-field scattering spatial distributions for the film, tip and tip-film configurations.

illumination-collection mode [33]. Aiming at understanding the far-field scattering properties of the asymmetric tip-tilted TES system, we calculated the dependence of the scattering patterns on the tilt angle of the tip, as shown in Figure 4A–E, where $R = 20$ nm, $\beta = 20^\circ$, $d = 1$ nm and $\gamma = 90^\circ$, respectively. The far-field intensities are normalized by that of $\alpha = 15^\circ$. In the case of $\alpha = 0^\circ$, the scattering pattern shows an isotropic ring implying weak directivity. Once the tip is tilted, we observe obvious directional scattering, as shown in Figure 4B–D. The emission angles of the maximum scattering are $(\theta, \varphi) = (-26^\circ, 180^\circ)$, $(-20^\circ, 180^\circ)$ and $(0^\circ, 180^\circ)$, respectively. When $\alpha = 60^\circ$, the scattering pattern presents two asymmetric lobes at $(\theta, \varphi) = (-26^\circ, 180^\circ)$ and $(15^\circ, 0^\circ)$, thus indicating weak directionality. To quantitatively provide the change of far-field scattering intensity, Figure 4F shows the dependence of the far-field intensity on the emission angle θ ($\varphi = 0^\circ$ or 180°). For the vertically placed tip of $\alpha = 0^\circ$, we observe two equivalent extremum peaks showing a maximum emission intensity of 5.7×10^{-9} . When we change the tilt angle α from 0° to 15° , the left peak intensity increases while the right peak intensity decreases sharply due to the blocked tip. The

strongest scattering intensity can be achieved with a tip tilt angle of 15° , which leads to an optimal emission angle of $\theta = -26^\circ$ and the maximum intensity of 7.1×10^{-9} . Further increasing α to 45° , the left peak intensity decreases while the right peak disappears absolutely. It is also clear that the maximum emission angle changes from -26° to 0° as α increases from 15° to 45° . When $\alpha = 60^\circ$, we observe an extreme peak at the emission angle of $\theta = 15^\circ$ with a higher relative intensity than that of peak at $\theta = -26^\circ$. In this case, the tip blocks the scattered photons from the right side. According to the calculated results, one may choose the objective with a suitable numerical aperture and the optimal collection orientation for achieving the high collection efficiency of TES.

More quantities were calculated to study the far-field scattering properties of TES where the tilt angle of the tip was fixed at $\alpha = 15^\circ$. Published studies have demonstrated that the morphology of TES tip has an important effect on the near-field enhancement and spatial resolution [34, 35]. For this reason, it is important to study the dependence of the far-field scattering pattern on the cone angle and the curve radius of the tip. Figure 5A shows that the maximum

Figure 4: Calculated far-field intensity versus tilt angle of the tip.

(A)–(E) The angular distribution patterns of the far-field intensity ($|E|^2$) in the TES system. The far-field intensities are normalized by that of $\alpha = 15^\circ$. (F) The angle-resolved emission pattern of the TES at different tilt angles of the tip (α).

Figure 5: Calculated far-field intensity versus emission angle, cone angle, tip radius, tip-film distance and dipole orientation.

The angle-resolved emission pattern of the TES at different (A) cone angles of the tip β , (B) tip radius R , (C) tip-film distance d and (D) dipole orientation γ . Inset: the enlarged image for $d = 8, 15$ and 20 nm in (C).

far-field intensity is improved sharply when the cone angle of the tip β increases from 10° to 40° . For the case of $\beta = 40^\circ$, we observe the strongest far-field intensity of 1.0×10^{-8} , which implies larger TES sensitivity. Further increase of β can decrease the scattering intensity. Furthermore, the maximum emission angle gradually changes from -26° to -17° as β improves from 10° to 60° . As shown in Figure 5B, when we change the curve radius R from 20 to 50 nm, the far-field intensity increases rapidly. The largest intensity of 2.4×10^{-8} can be achieved with $R = 50$ nm. Further increasing the tip radius can decrease the intensity. The reason for this variation tendency can be explained by an AFM tip above the Au substrate [36]. More importantly, the far-field intensity is at the same order of magnitude for R between 30 and 60 nm. Hence, one may choose a tip with a smaller radius to obtain a relatively higher spatial resolution without sacrificing much intensity. Furthermore, the emission angle remains unchanged with the increase of the tip radius, thus implying that the tip radius has no influence on the emission orientation of the TES [37].

The tip-substrate distance was set as $d = 1$ nm in all calculations in order to provide strong near-field coupling

in the nanogap between the tip and the substrate. Such an electromagnetic field coupling may offer enhanced far-field intensity, thereby improving the TES sensitivity. To understand the tip-substrate coupling effect, we calculated the dependence of the far-field intensity on the distance d , as shown in Figure 5C. To provide a better view, the inset shows the enlarged image for $d = 8, 15$ and 20 nm. Clearly, the maximum far-field intensity decreases sharply and the peaks do not shift with the increase of the tip-substrate distance from 1 nm to 20 nm [38]. We can conclude that the near-field coupling between the tip and substrate can significantly influence the far-field scattering intensity but not the emission orientation of the TES signal.

Apart from the TES configuration, the contributions of the molecular concentration and dipole orientation to the far-field properties cannot be ignored. Especially in single molecule studies, the dipole orientation plays an important role in TES [39]. We calculated the dependence of the far-field intensity on the dipole orientation γ , where the excited molecule was modelled as an electric dipole, as shown in Figure 5D. As increasing γ from 0° to 90° , the far-field intensity increases sharply and is at the same order

of magnitude for $\gamma > 45^\circ$. The strongest far-field intensity of 7.1×10^{-9} can be achieved when $\gamma = 90^\circ$, which coincides with the dominant coupling orientation between the tip and substrate. Similarly, the dipole orientation has no effect on the emission angle.

4 Conclusion

In this paper, the tip-tilted side illumination-collection TES configuration was proposed and studied. The underlying physical mechanism of the high directional emission of TES was deeply analyzed by studying the far-field interference between the LSPR and SPP modes. We systematically investigate the dependence of the far-field scattering properties on the tip morphology, the tip-substrate distance and the molecular dipole orientation. The tilted tip presents high directional scattering characteristic compared with the vertically placed tip, implying larger collection efficiency and TES sensitivity. The emission angle can also be controlled by changing the tilt angle and the cone angle of the tip. Furthermore, the tip shape, near-field coupling between the tip and substrate and molecular dipole orientation can significantly modify the far-field scattering intensity. The optimal tilt angle and cone angle of the tip are 15° and 40° , respectively, demonstrating maximum emission intensity of 1×10^{-8} at an emission angle of 22.5° . When the molecular dipole orientation coincides with the dominant coupling direction of the tip and substrate, the emission intensity achieves its maximum. The best tip radius is between 30 and 60 nm and a sharper tip can be chosen to obtain a higher spatial resolution. The findings of this study can be used as a guide in the construction of the TES instrument with high sensitivity.

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