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Local field enhancement of an infinite conical metal tip illuminated by a focused beam

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We present a systematic numerical investigation of conical metal tips which are commonly used in tip-enhanced Raman spectroscopy (TERS). Different from previous studies, we focus on how the tip length and the illumination condition influence the local field enhancement at the tip apex, and provide a useful reference for real experiments. In particular, we show that the type of illumination has a dramatic influence on the field enhancement: a localized illumination spot – as used in experiments – producing a very different response than a plane wave illumination – as usually used in previous models. Also, the effect of the different geometrical parameters, such as the sharpness of the tip apex and the cone angle, provides guidance to optimize the tip design. Finally, we investigate the influence of the substrate and compare numerical data with results deduced from a simplified model, finding good agreement. This brings new insights into the enhancement mechanism of TERS. Copyright © 2009 John Wiley & Sons, Ltd.

Keywords: tip-enhanced Raman spectroscopy; surface-enhanced Raman spectroscopy; localized plasmon resonance; lightning rod effect

Introduction

Tip-enhanced Raman spectroscopy (TERS) is a near-field spectroscopic technique measuring both the topographic information and Raman spectrum with nanometer spatial resolution using a sharp metal tip.[1] The tip apex functions as a single 'hot' spot, which enhances the Raman scattering from the scanned sample area. At optimized conditions, single-molecule sensitivity[2] can be achieved and the spatial resolution can reach $\sim$10 nm,[3] making TERS an important candidate for nanoscale chemical analysis. Since the first reports in 2000,[1,4,5] TERS has been successfully implemented in different disciplines, such as life science,[6,7] material science,[8] surface science,[9] etc. Besides these applications, TERS has also been used to study some of the most fundamental aspects of its cousin technique, surface-enhanced Raman spectroscopy (SERS), especially the properties of the 'hot' spot in SERS, since TERS is playing with a single 'hot' spot and can collect both the topographic information and the Raman spectrum simultaneously. Thanks to these merits, TERS has provided a direct proof for single-molecule Raman detection,[2,10–12] an issue debated for almost 10 years in the SERS community. Furthermore, TERS also allows us to investigate the detailed physical properties of the 'hot' spots, such as the influence of nanometer-scale corrugation on the field enhancement[13] and thermal effects at the 'hot' spot.[14] Despite these achievements, our understanding of the enhancement mechanisms of TERS is still superficial. In particular, the single nanoparticle model is usually used to interpret TERS experiments,[15] although it is very different from real experiments, in which an infinite conical tip and a substrate are used.

As one of the most notable features of the metal tip, the infinite tip length makes the enhancement mechanisms of TERS fundamentally different from those of SERS, the latter being well understood within the framework of localized plasmon resonances (LPRs) of nanoparticles.[16] In the last few years, simulations have been reported on TERS based on different numerical methods.[17–21] Most of them use truncated tips and focus on how the local geometrical parameters of the tip apex influence its local field enhancement. However, as a nanowire, a TERS tip can guide, 'focus' surface plasmon polaritons (SPPs) propagating on its flank, and consequently enhance the local electric field at the tip apex.[22,23] It is important to investigate the impact of such delocalized effects at the tip apex. Besides the infinite length, the illumination is also an important issue in TERS. Previous theoretical studies only consider the case of plane wave illumination, which is very different from real experiments where the laser beam is tightly focused on the tip apex. This may cause significant deviations of the simulation result from the real experimental result. Actually, it was recently reported that, even for a single spherical nanoparticle, the optical response under different illuminations can be different.[24] Another dramatic example was reported by Ditlbacher *et al.*[25]: it shows that the SPP modes on a long metal nanorod can be excited with a focused beam only when the rod end is illuminated. In the case of TERS, the shape of the tip is much more complicated than a spherical particle, the size is also much larger, and consequently the illumination could play a significant role.

In addition to the issues related to the tip length and the illumination condition, we also need to consider the influence by the substrate, which is always present in practice. It has been experimentally demonstrated that varying the substrate can dramatically change the field enhancement at the tip apex.[9,26] With a Au substrate, the electric field intensity can be enhanced by two orders of magnitude, and even single molecules can be

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detected. If the substrate is changed to Pt, still a metal, the enhancement drops. For a semiconductor or dielectric substrate, e.g. Si or glass, the field enhancement decreases further and is even one order of magnitude lower than in the case of a Au substrate. In these conditions, it becomes a challenging task to obtain a reasonable signal from small molecules. Although simulations have been reported,[20] there is still lack of clear rules to describe and predict the substrate effect in TERS. This has become an obstacle for the application of TERS in specific areas, such as material science, in which a broad variety of substrates is encountered.

In this work, we systematically investigate the local optical response at the tip apex of conical Ag tips, in order to understand (1) how the tip length determines the field enhancement and (2) how the tip shape modulates the local field intensity. Moreover, we investigate how the presence of a substrate influences the field enhancement, with the attempt to provide a simple model to predict the enhancement as a function of the optical constants of the substrate.

Model

Conical tips with a rounded apex are investigated in this work as shown in Fig. 1(b). The tip shape is determined by three independent parameters: the cone angle α, the apex radius r, and the tip length l. The radius r determines the local geometrical feature of the tip apex, while the overall tip shape is given by the cone angle α.

A commercial finite-element method solver (Comsol Multiphysics) is used in this work to solve Maxwell's equations. In the simulation, Ag is considered as the tip material; the optical constants measured by Johnson are used.[27] The tip apex is meshed with a step of 0.5 nm in order to obtain accurate results, as shown in Fig. 1(a). Axial symmetry is used in order to reduce the memory requirement and the computing time. Perfect matched layers (PMLs) are set up to terminate the metal tip and mimic infinite space. As previously mentioned, using a focused beam illumination instead of a plane wave is important for appropriate simulation of real TERS configurations. In this work, we create a focused spherical wave by putting a series of magnetic current sources on the equal phase surface of a spherical wave. Based on Huygens principle, the total field generated by the sources forms a tightly focused spot, as shown in Fig. 1(c). The illumination angle and numerical aperture (N.A.) of the beam can be tuned by adjusting the geometrical parameters of magnetic current sources. In this work, an N.A. = 0.5 is used. Since the radiation of a current source can also be influenced by the presence of a structure in its vicinity, we position the sources more than three wavelengths away from the tip, to avoid any undesired effect.[28] Furthermore, the radiation power from a current source also depends on the frequency and this effect was supplemented by normalizing the data with the radiation power spectrum in free space. Let us point out that this axial symmetrical illumination scheme is very similar to the parabolic mirror-based TERS setup, which has been successfully demonstrated by Steidtner and Pettinger.[26]

Results and Discussions

Tip length effect

As previously discussed, the optical behavior of an infinitely long tip is different from that of a common SERS substrate, which is mainly dictated by the LPR of nanoparticles or particle aggregates. To understand this difference, we simulate tips with different lengths (200, 500, 1000, 2000, 3000 nm and infinitely long) (Fig. 2). When the tip is only 200 nm, three peaks are observed in the spectrum; they correspond to the LPRs of the tip, similar to normal metal nanoparticles. When the tip length increases to 500 nm, additional peaks appear because of the excitation of higher order resonances. For tips of 1000 nm and longer, the resonance peaks become weaker and periodic in the red-infrared (IR) regime. When the tip is infinitely long (terminated by a PML layer 4.5 μm away from the tip apex), the resonant peaks in the spectral range $\lambda > 400$ nm totally disappear and only a flat spectrum remains.

There are two causes for the above-described transition from a short tip to a long tip: (1) the size of the focus spot and (2) the traveling SPPs on the tip. When the tip is short (smaller than the focus spot), the light drives the conducting electrons in the metal tip in phase and generates collective oscillations (i.e. LPRs). As a result, the contributions from individual electrons build up and generate a strong local electric field at the tip apex. For a long tip, the focus spot is smaller than the tip length and there are no such collective electron oscillations in the whole tip. Instead, the illumination at the tip apex causes two different types of excitations: LPRs, which are mainly concentrated at the tip apex, and SPPs, the delocalized modes. The LPRs store the electric field energy in the vicinity of the tip apex and appear as resonance peaks in the near ultraviolet and blue range. On the contrary, SPPs as delocalized modes can propagate along the tip. When the SPPs meet the ends of the tip, they are reflected and form cavity modes. Consequently, periodic peaks appear in the field enhancement spectrum when the tip length is more than 1 μm

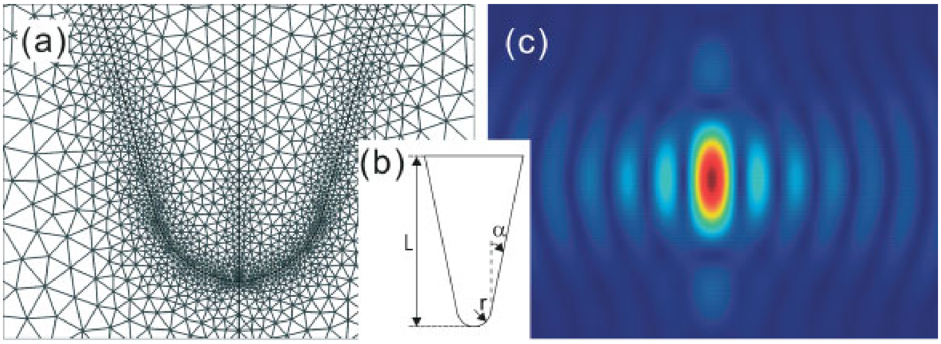

Figure 1. Tip model used for the simulation. Panel (a) shows the triangular mesh at the tip apex. The tip geometry is described in panel (b). Panel (c) shows the focused beam used for illumination.

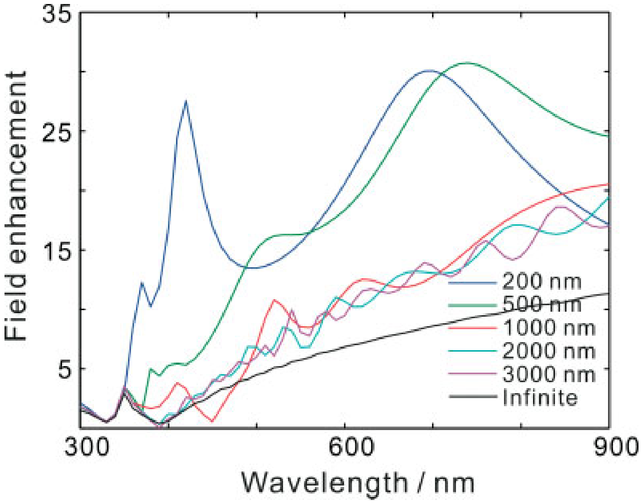

Figure 2. Electric field amplitude enhancement spectra for conical tips with different tip lengths *l*. The tip radius *r* is 20 nm and the tip angle α is 15°.

(Fig. 2). Meanwhile, since the cross section of the tip changes along the axis and the propagating SPPs see heavy losses, these SPP-induced resonances are weaker than those associated to the in-phase excitation in the case of a short tip. Nevertheless, it is still possible to use these SPPs to enhance the local electric field at the tip apex. In fact, this idea has recently been proposed by Stockman,[22] who pointed out that the propagating SPPs can be concentrated and enhanced with a tapered tip.

In order to investigate the difference between the case of a plane wave excitation and the case of a focused beam excitation, a 2-μm-long tip is tested under both types of illuminations in Fig. 3. A highly localized and enhanced electric field is observed at the tip apex in both cases. However, the field distributions in the vicinity of the tip body are different. With a focused beam, the field intensity drops rapidly away from the tip apex. At the truncation plane, the electric field becomes negligible. In the case of a plane wave excitation, the whole tip is illuminated and driven as one oscillating dipole, resulting in high field intensity at both the tip apex and the truncation plane. Figure 3 illustrates how significantly the illumination conditions can influence the simulation results – in particular the field enhancement – for a structure longer than a wavelength.

From the above discussion, we learn that an appropriate illumination in TERS models is crucial for obtaining experimentally meaningful results. Furthermore, the simulations indicate that, when illuminated by a focused beam, a smaller particle produces a better enhancement compared to a long tip because the collective movement of the carriers can be excited in the case of the nanoparticle.

Tip sharpness influences the field enhancement

It is well known that for an ideally sharp metal cone, the apex represents a field singularity and generates an infinitely strong electric field, the so-called lightning rod effect.[15] As a result, a sharper tip apex is closer to such a singularity and produces a stronger field enhancement. In fact, this has been clearly seen during the evolution of TERS over the last 5 years. Small molecules have only become visible once the fabrication methods for producing extremely sharp Au and Ag tips became available.[29] Besides sharpening the tip, another way to increase the enhancement is to increase the wavelength of the illumination, since the sharpness refers to the relative dimension between the radius of curvature of the tip apex and the wavelength. However, to the best of our knowledge, nothing has yet been reported in this direction because the sensitivity of the detectors is generally much lower in the IR regime than in the optical regime.

To study how the sharpness of the tip apex influences the near-field spectral response, a series of infinite tips with different apex radii *r* and fixed cone angle α are simulated (Fig. 4). It is worth mentioning that the high field intensity caused by the geometrical singularity (lightning rod effect in this case) does not show any resonant behavior, in contrast to the plasmon-induced enhancements. In fact, both types of enhancements can be observed in Fig. 4. At $\lambda = 350$ nm, the peak is caused by the local plasmon excitation at the apex, while the flat and strong enhancement curve in red and IR regimes are mainly caused by the lightning rod effect.

These two types of field enhancements depend on the apex radius in different ways. In the case of the LPR-induced field

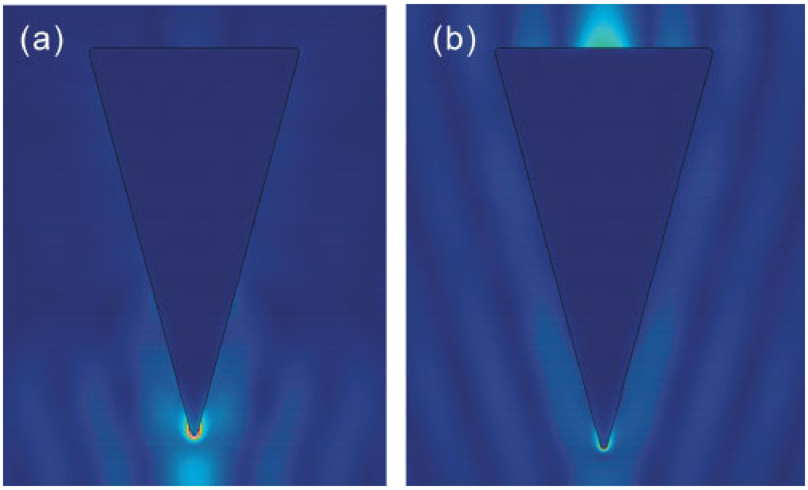

Figure 3. Electric field intensity maps of a truncated tip under different illuminations. Panel (a) and (b) represent illumination by a focused beam and a plane wave, respectively. Tip length $l = 2000$ nm, tip angle $\alpha = 15°$ and tip radius $r = 20$ nm.

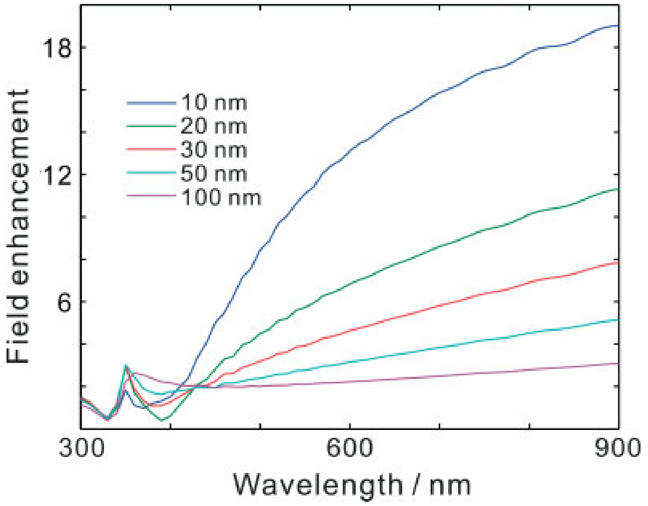

Figure 4. Local electric field amplitude enhancement spectra at the tip apex for different apex radii. The tip length is infinite and the tip angle $\alpha = 15^\circ$.

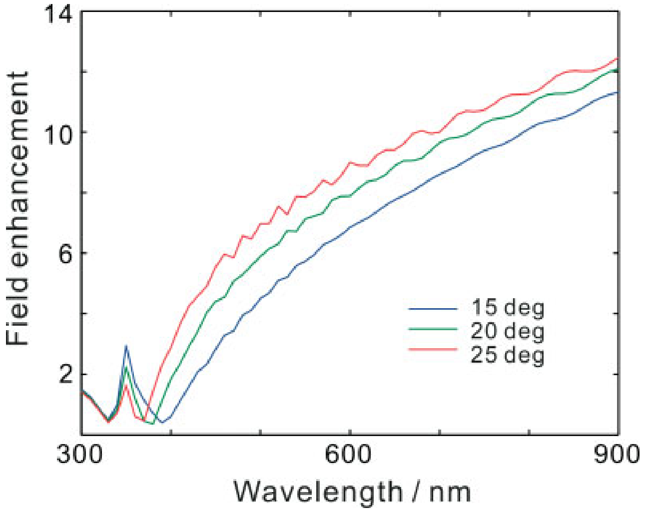

Figure 5. Local electric field amplitude enhancement spectra at the tip apex for different tip angles. The tip length is infinite and the tip radius $r = 20$ nm.

enhancement, when the apex radius r increases, the resonance becomes broader; when r reaches 100 nm, the resonance shows a clear red shift. These behaviors are similar to those of spherical particles. Moreover, there is no explicit relation between the field enhancement and the apex radius in this case. For the lightning rod effect, there is no resonant behavior and the enhancement rapidly increases when the tip radius decreases. This effect has also been observed by Downes *et al.*[30] However, their results show complicated resonance features instead of a rather flat electric field enhancement spectrum. This might have been caused by the truncation of the tip and the different illumination mode used in their simulation. One interesting phenomenon in Fig. 4 is that the enhancement increases dramatically when r decreases from 20 to 10 nm. In other words, a slight improvement of tip sharpness will lead to a significant increase of the field enhancement. This could explain the different results reported by two independent groups, in which the Raman spectra from similar molecules were very different.[10,11] The tips used by Neascu *et al.*[11] have an apex diameter $r \sim 10$ nm, while in the case of Domke *et al.*,[10] r was >20 nm. This variety could cause a twofold difference in the field enhancement and consequently a fourfold difference in the heat generated by ohmic loss. Considering that a thinner tip is less capable of dissipating heat, the local temperature at the apex of the $r = 10$ nm tip can be much higher than in the case of the $r = 20$ nm tip. This may have a significant influence on the Raman spectra.[31]

Effects from the cone angle

The tip angle also influences the field enhancement. In this work, we simulate tips with cone angles from 15 to 25°, a range which is practical for electrochemical etching methods.[32] The results are shown in Fig. 5. All the three spectra exhibit a similar profile: (1) there is a resonance at $\lambda = 350$ nm (LPR-induced enhancement) and (2) they provide a good enhancement in the IR range (lightning rod effect). The only difference is that the tip with a larger cone angle has a slightly higher field enhancement in the IR regime. This phenomenon is similar to the behavior of biconical antennas, whose impedance slightly decreases (the local field enhancement is better by virtue of the reciprocity principle) when the cone angle increases.[33] If we consider that the biconical antenna is a simple combination of two single cones, we can understand the phenomenon that the tip with a larger cone angle generates a larger field enhancement. It is, however, worth noticing that this biconical antenna is very different from an individual tip and can only serve as a simple model for understanding this cone angle effect, since the antenna still seems to function at optical frequencies.[34]

Substrate effect

The optical response of an isolated TERS tip has been discussed in the previous sections. However, in practice, close to the tip apex there is always a substrate that can influence the local optical response in a dramatic way. Our strategy for studying this substrate effect is to monitor the local electric field enhancement as a function of the optical parameters of the substrate (the other parameters, such as the geometrical parameters of the tip and the illumination wavelength are fixed). In order to reduce computation time, a short tip (1 μm truncated tip instead of the infinite one) is considered. Since we wish to concentrate on the influence of the substrate, an effect mainly localized on the near-field vicinity of tip–sample junction, this model will not cause any major discrepancy on the result.

Figure 6 shows the electric field enhancement as a function of the optical constant of the substrate at $\lambda = 633$ nm (similar results are also obtained at other wavelengths, $\lambda = 488$, 532 and 785 nm). The most prominent feature of this map is that the enhancement exhibits both the maximum and minimum values when the permittivity of the substrate is close to 0. This phenomenon can be explained with the simple model of a dipole above a planar substrate.[35] In this context, we model the tip as a single oscillating dipole with a polarizability $\alpha = 4\pi a^3(\varepsilon_t - 1)/(\varepsilon_t + 2)$, where a represents the apex radius of the tip, and ε_t is the complex permittivity of the tip. The image dipole of the tip created by the substrate is $\alpha\beta = \alpha(\varepsilon_s - 1)/(\varepsilon_s + 1)$($\varepsilon_s$ is the complex permittivity of the substrate). Then, the total polarizability can be written as:[36]

$$\alpha_{\text{eff}} = \frac{\alpha(1+\beta)}{1 - \dfrac{\alpha\beta}{16\pi(a+z)^3}} \tag{1}$$

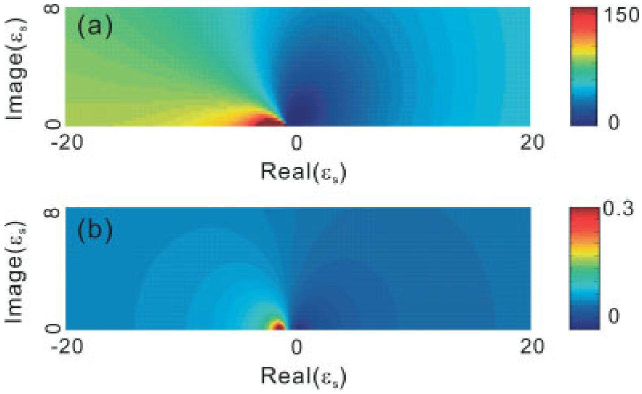

Figure 6. Influence of the substrate on the electric field enhancement. (a) Enhancement map at the tip apex as a function of the substrate permittivity. Tip radius $r = 20$ nm, tip length $l = 1000$ nm, tip radius $\alpha = 15^\circ$ and tip-substrate distance 1 nm. (b) Effective polarizability map of a dipole 1 nm above an infinitely large substrate as a function of the permittivity of the substrate.

where z is the tip–substrate distance. Hence, the local enhanced field can be directly plotted using Eqn (1), as shown in Fig. 6(b). The comparison between the two maps in Fig. 6 indicates a remarkable similarity. In both maps, the intensity reaches the maximum and minimum in the area where $\varepsilon_s \approx 0$. This can be well understood by considering the role of the image dipole. When ε_s approaches -1, the polarizability of the image dipole goes to infinity; when ε_s is close to 0, the image dipole almost cancels the original dipole totally and, consequently, the enhancement reaches a minimum.

In the area far from $\varepsilon_s \approx 0$, the enhancement map is rather smooth. Especially, the field enhancement tends to be constant when the substrate is a good conductor ($\mathrm{Re}(\varepsilon_s) \ll -1$, $\mathrm{Im}(\varepsilon_s) \sim 0$). This can also be explained by the fact that the image tip becomes similar to the real tip when the metal is close to a perfect mirror (i.e. a perfect conductor). More importantly, in this region the field enhancement remains high. The enhancement drops slowly when $\mathrm{Im}(\varepsilon_s)$ increases. This property should be kept in mind by surface chemists who use TERS to investigate catalysis reactions on different metals. According to this enhancement map, one can always use IR light to obtain a reasonable enhancement, since all metals become good conductors in this regime.

In real experiments, it is difficult to fabricate a perfect conical tip or a perfectly smooth substrate. Defects are often present at the tip apex or on the substrate, and may change the near-field optical response of the tip. Recently, this effect has indeed been reported in both tip-enhanced fluorescence spectroscopy and TERS studies.[13,37] Therefore, further work is still needed in order to fully understand these details.

Conclusions

In summary, we have numerically investigated the local optical responses at the apex of conical Ag tips. It is found that properly setting the illumination in the model is crucial to obtain an experimentally meaningful result. Our simulation also reveals a dramatic difference of the field enhancements between short and long tips: a short truncated tip can produce a better enhancement than a long one because of the excitation of the LPRs. Moreover, we have investigated the influence of apex radius r of the tip. A significant improvement of the field enhancement is observed when r decreases from 20 to 10 nm. This provides a possible explanation for the discrepancy observed among tip-enhanced Raman spectra recorded by different groups. Finally, the substrate effects in TERS experiments have been analyzed. We find that the influence from the substrate can be well understood by simply considering the role of the image tip in the substrate.

Acknowledgement

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