Tuning the resonance frequency of Ag-coated dielectric tips

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Abstract: A finite element model was built to investigate how to optimize localized plasmon resonances of an Ag-coated dielectric tip for tip-enhanced Raman spectroscopy (TERS). The relation between the resonance frequency, the electric field enhancement and the optical constant of the dielectric tip was numerically investigated. The results show that increasing the refractive index of the dielectric tip can significantly red shift the localized plasmon modes excited on the Ag-coated dielectric tip, and consequently alter the field enhancement. Moreover, the influence of the width of the resonance on the Raman enhancement was also considered. When taking all the factors into account, we find that an Ag-coated low-refractive index dielectric tip provides the best Raman enhancement in the blue—green spectral range. This is consistent with our prior experimental results.

OCIS codes: (000.4430) Numerical Approximation and Analysis; (999.9999) Near-Field Optics; (240.6490) Spectroscopy, surface; (300.6450) Spectroscopy, Raman; (999.9999) Finite Element Method

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1. Introduction

Tip-enhanced Raman spectroscopy (TERS) is a promising technique for nanoscale analysis, because of its capacity of providing rich chemical information [1, 2], high spatial resolution [3] and high sensitivity [4-6]. TERS is essentially based on the strongly enhanced electromagnetic field excited on the apex of a sharp metallized tip [7, 8]. According to mechanistic studies on surface-enhanced Raman spectroscopy (SERS), this field enhancement has two origins: resonant excitation of the localized plasmons (LPs), and the sharp-edge induced 'lightning rod' effect which confines the electric field to the tip apex [9]. From this point of view, an adequate fabrication technology for properly shaping the sharp metal tip, which enables the presence of strongly localized modal fields at a chosen resonance frequency, holds the key for successful TERS. Among all types of TERS tips, metal-coated dielectric tips, such as, Ag-coated atomic force microscope (AFM) tips are a popular choice, because of two reasons. First, AFM is widely accessible in different laboratories. Secondly, AFM is a robust and versatile imaging technique, affording more information than only topographic images, e.g., friction force etc [10]. This provides valuable complementary information for material analysis. So far, several methods have been developed to fabricate the Ag-coated AFM tips [1, 2, 11], and interesting applications on carbon nanotubes have also been demonstrated [12]. However, the reproducibility to obtain a high performance TERS tip, a so-called 'hot' tip, is still poor, often due to the spectral mismatch between the laser excitation and the resonance frequency of the tip [13]. Today, this low yield of 'hot' tips has been a major bottleneck for TERS to be developed into a robust analytical technique.

There are two possible solutions for matching the plasmon resonance of the Ag-coated dielectric tip with the wavelength of the excitation source: (1) scanning the wavelength of the light source; (2) tuning the resonance frequency of the tip. At a first sight, the first approach seems more straightforward. However, excitation wavelength scan is expensive and inconvenient for TERS: a multi-wavelength laser source is needed; notch filters for the different laser lines and a Raman spectrograph covering a wide spectral range are required. The second approach is more practical: only one fixed laser line and one notch filter are required. It is well known that the resonance of LPs on a metal nanostructure is sensitive to its shape and the optical properties of its surrounding materials [14-16]. From this point of view, the mismatch between the laser source and the resonance frequency of the Ag-coated tip is caused by the improper choice of the tip shape and the underlying material. Therefore, the solution to the problem lies in tuning the resonance by changing the accessible parameters of the metallized tip.

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Recently, it was reported that the Ag-coated dielectric tips with different refractive indices give different Raman enhancement [13, 17]. Following this idea, the performance of Ag-coated AFM tips has been significantly improved by using low refractive index AFM tips. However, the experiment was only performed for a 488 nm illumination with a limited number of AFM tips. The details for this material dependent enhancement are still unclear. We therefore systematically investigate how the optical properties of the AFM tip influence the resonance properties of the Ag coating, such as the resonance frequency, the resonance width and the associated field enhancement (i.e. the resonance amplitude). Furthermore, the physics behind the simulation is also discussed.

2. Simulation

In this work, an Ag-coated axis-symmetric tip was simulated as shown in Fig. 1. A dielectric tip with a rounded end (10 nm diameter) was used to model the dielectric AFM tip. The shape and size correspond to the geometric parameters of commercial AFM tips. The Ag coating was modeled by a 20 nm thick homogeneous layer on the top of the dielectric tip. Since only the p-polarization component of electric field (along the tip axis) can be greatly enhanced [7, 8], a TM mode incident light beam (***E*** is parallel to the tip) was employed. An important issue for the simulation of Ag nanostructures is the optical constants, which can be different from those of the corresponding bulk material when their sizes are smaller than 5 nm [18, 19]. Since the thickness of the Ag layer in our model is relatively large (20 nm), measured data from bulk silver was directly used without further considering the negligible size-induced effect [20].

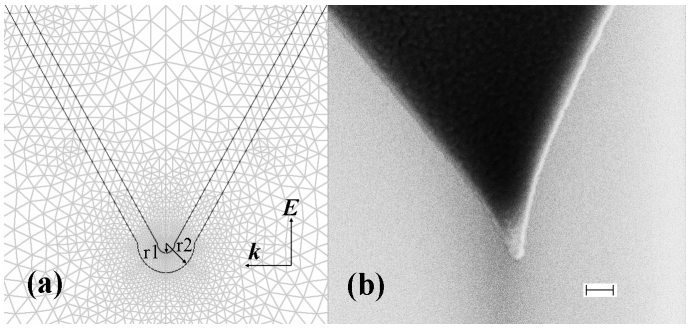

Fig. 1. (a). Dimension size and mesh of the tip used for the simulation. Here, r_1=10 nm, r_2=30 nm. (b) SEM picture from side-view. The scale bar denotes 100 nm.

For the numerical analysis, a finite element method (FEM) based tool integrated in the COMSOL Multiphysics package was employed to solve the Maxwell equations [21]. Because in of FEM simulations, any infinite structure has to be truncated by the boundary condition to obtain a tractable computation window, we terminated the support of the tip at the length of 550 nm. A significant reduction in computational costs and memory requirements is achieved by taking axis-symmetric boundary conditions into account. To get reliable data, the boundary conditions were carefully chosen: because FEM is a domain method requiring the discretization of the entire field domain, absorbing boundary conditions (ABCs) must be implemented for simulating an open space. In this work, the ABCs were applied with a 500 nm (larger than the half wavelength) distance from the tip to avoid an unphysical result caused by inefficient adsorption of the evanescent components of the scattering field. Scattering boundary conditions were then used on the top and bottom of the simulated space. To reduce spurious reflections, especially from the radial corners, fictitious perfectly matched layers (PMLs) were added proximately to the outer side of the scattering boundaries.

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3. Results and discussion

Figure 2 depicts the calculated distribution of the electric field strength at the tip apex for p-polarized excitation. As expected, the p-component of the electric field is strongly enhanced as it has been also observed for pure Ag tips by other groups before [7, 22].

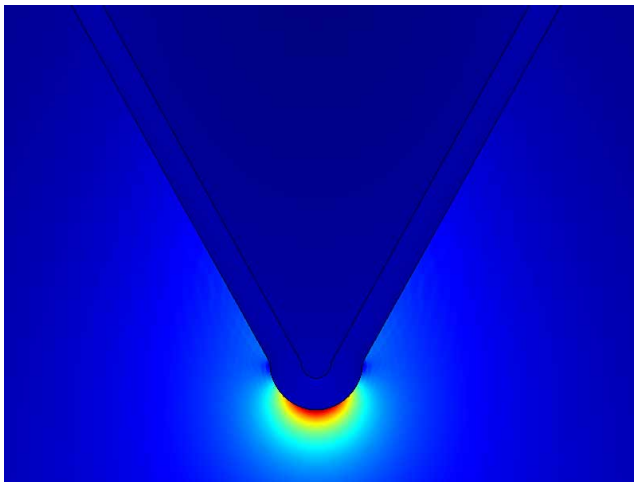

Fig. 2. Calculated electric field distribution of the *p*-component.

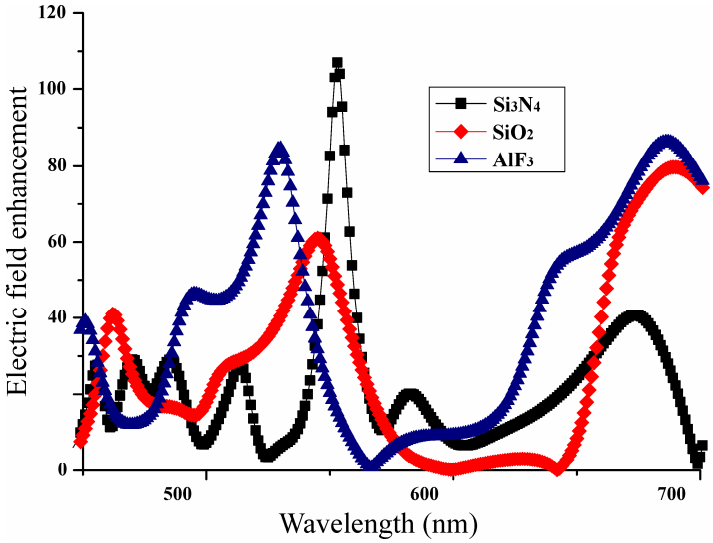

Fig. 3. Spectral responses of the field enhancement for an Ag coated Si_3N_4 tip, glass and AlF_3 tip.

3.1 How does the refractive index influence the resonance behavior of an Ag-coated dielectric tip?

To study the resonance behavior of Ag-coated AFM tips, we calculated the spectral characteristics of the LP resonances for three different AFM tips (Si_3N_4, glass and AlF_3 tips). Figure 3 shows the spectral responses of field enhancement for these three material systems. A complicated resonance structure is observed from the Ag-coated Si_3N_4 tip. Its most pronounced resonance peak is in the green range (about 550 nm), while there are other weak resonances in a wide spectral range. For the Ag coated glass and AlF_3 tip, there are mainly two broad and strong resonances in the visible light range: 450–550 nm and 640 nm–near

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infrared. Comparing these three tips, the field enhancement of the Ag-coated glass and AlF_3 tip is generally higher than that of the Si_3N_4 tip in the blue—green spectral range, and consequently, will provide a higher Raman enhancement in this spectral range.

The prediction above is consistent with our previous experiments performed with 488 nm excitation [13, 17]. The enhancement factor of an Ag-coated silicon nitride tip was rarely larger than 5, while an Ag-coated glass tip, or an AlF3 modified tip can afford much larger enhancement (>10 times).

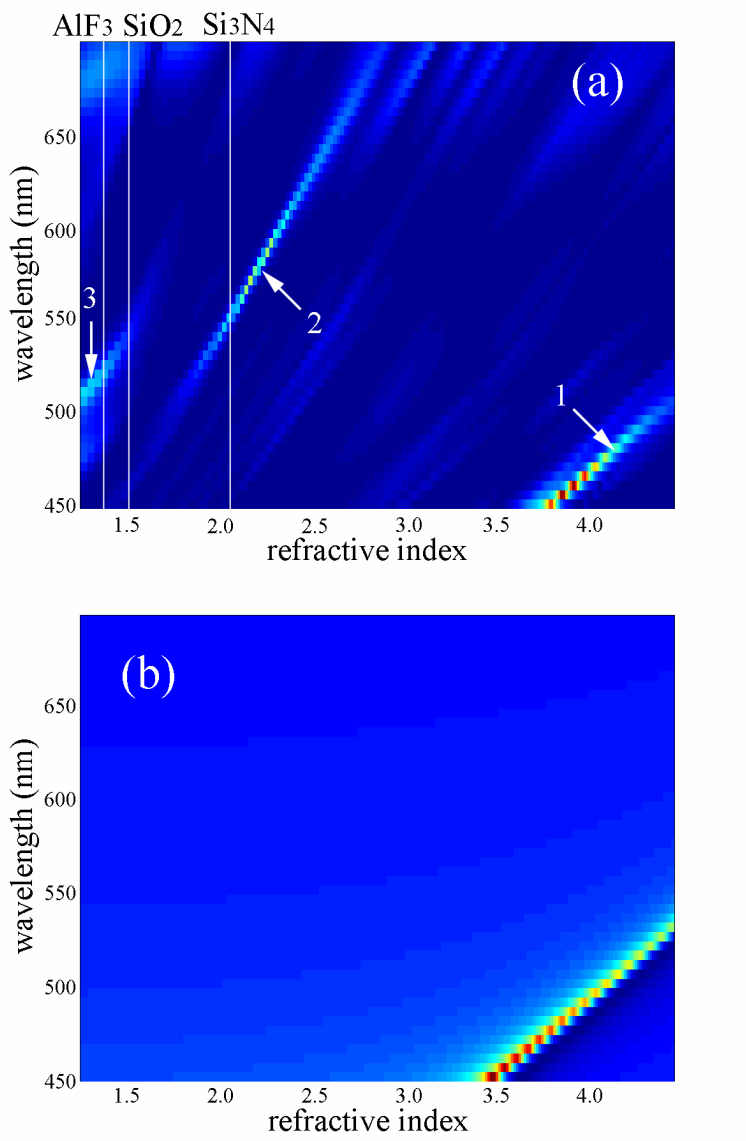

Fig. 4. (a). Field enhancement against the refractive index and the wavelength (i.e. as two dimensional intensity plot) to reveal the resonance behaviors of the Ag-coated AFM tip. (b) The same plot for an Ag coated spherical particle. In these two plots, dark blue and deep red represent the lowest and highest intensities respectively.

However, from Fig. 3, it is not clear how the LP modes of the Ag-coated tip are related to the optical constant of AFM tip, e.g. what the relation is between these three spectral

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responses, how the dielectric constant shifts the LP modes, etc. Therefore, we plotted in Fig. 4(a) the field enhancement against the refractive index and the wavelength (i.e. as two dimensional intensity plot) to reveal the characteristics of the resonance modes. It is clear that the resonance modes which are responsible for the field enhancement can emerge, shift, broaden and disappear along the axes of refractive index. The spectra corresponding to the three aforementioned tips are labeled in that plot, clearly showing the relations between the resonance peaks shown in Fig. 3: the resonant enhancements of the electric field on the Ag-coated glass tip and Ag-coated AlF_3 tip are induced by the same resonance mode [mode 3 in Fig. 4(a)] with a spectral shift of ~20 nm, while the enhancement of the Si_3N_4 tip is generated by other resonance mode [model 2 in Fig. 4(a)].

One of the most prominent features in the plot [Fig. 4(a)] is that all the resonance modes are red shifted with an increasing refractive index of the AFM tip. However, the resonance structure shown in Fig. 4(a) is complicated due to the geometrical complexity of the tip. To exclude the intricacy induced by the geometrical reasons and further understand the origin of this material-dependent red-shift effect, we simplified our tip model to an Ag-coated spherical particle, which is ideal in terms of geometry, analytically accessible and well studied [18, 19]. We assume that the particle is much smaller than the excitation wavelength, and consequently, the quasi-static model is feasible. If the core diameter is R, and the thickness of the Ag coating is d, the static polarizability of this particle will be [18, 19]:

$$\alpha = \frac{4\pi}{3}\varepsilon_0 (R+d)^3 \frac{(\varepsilon_s - 1)(\varepsilon_c + 2\varepsilon_s) + (\frac{R}{R+d})^3 (\varepsilon_c - \varepsilon_s)(1+2\varepsilon_s)}{(\varepsilon_s + 2)(\varepsilon_c + 2\varepsilon_s) + (\frac{R}{R+d})^3 (\varepsilon_c - \varepsilon_s)(2\varepsilon_s - 1)} \quad (1)$$

Here ε_s and ε_c denote the permittivities of the shell and core materials, respectively. Using Eq. (1), a field-enhancement map was plotted again with $R/(R+d) = 1/3$ (a value corresponds to our tip model), as shown in Fig. 4(b). The LP mode set of this shell structure is explicit. There is only one resonance mode in the whole spectral range. It shifts to lower frequency (longer wavelength) with increasing the refractive index of the core material. This is exactly in accordance with the case of the Ag-coated dielectric tip shown in Fig. 4(a). Therefore, the core material induced resonance shift is rather a fundamental effect of such metal coated structures, no matter whether a structure is as simple as a spherical particle, or a much more complicated structure like the metal-coated dielectric tip.

Besides the resonance frequency, Raman enhancement is also dictated by the magnitude of the LPs excited on the Ag-coated tips. In Fig. 4(a), three resonance modes, marked by arrows, afford the strongest field enhancement. Mode 1 is the highest one. Unfortunately, it requires a high refractive index of the AFM tip, which is hard to be met by common materials. Mode 2 is also strong. However, the resonance is narrow (<20 nm), and consequently difficult to be matched to a fixed excitation laser line. Besides the difficulty of frequency-matching, a narrow resonance encounters other problems for TERS/SERS, which will be discussed below. Mode 3 is less enhancing comparing to modes 1 and 2, but it has some advantages: (1) the refractive index needed by this mode is around 1.4 – 1.5, which includes the value for glass; (2) its resonance is broad, over 40 nm, which is important for the aforementioned practical reasons.

The width of plasmon resonance is an important, but often neglected issue in area of TERS/SERS. In a large number of papers, the formula $A_{Raman} = A(\nu_L)^4$ is used for estimating the Raman enhancement (A_{Raman} is the enhancement of the Raman signal, and $A(\nu_L)$ denotes the enhancement of excitation field at a frequency ν_L). However, this is only an approximation of a more correct expression, $A_{Raman} = A(\nu_L)^2 A(\nu_S)^2$ [23, 24], with the assumption that $A(\nu_L) \sim A(\nu_S)$ ($A(\nu_S)$ is the electric field enhancement of the scattering light with a Stokes shift of ν_S). In the field enhancement plot shown in Fig. 4(a), this assumption is not always correct. The mode 2 is a clear example. Its resonance width is less than 20 nm in its most highly enhanced spectral range (500 nm – 650 nm). Considering a light source of 500 nm, the

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wavelength of a Ramam band with a Stokes shift of 1000 cm^{-1} (a typical vibrational frequency) will be 526 nm, 26 nm from the laser line. In other words, the assumption $A(v_L) \sim A(v_S)$ is no longer correct in this case, and the real Raman enhancement will be much lower than estimated by the formula $A(v_L)^4$.

Taking all these considerations into account, the most promising region of the whole field enhancement map for TERS applications is the low refractive index part (mode 3), where the magnitude of the resonance is relatively high and the width of the resonance is broad, covering the spectral range interesting for chemical analysis. This finding is in excellent agreement with what has been observed in the prior publication [17].

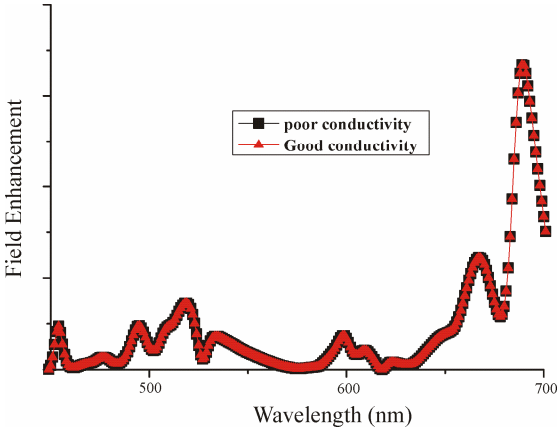

Fig. 5. Spectral response of the field enhancement for an Ag coated dielectric tip with different conductivities. The refractive index of the tip is 3.48, the conductivities of these two tips are 10^{-12} S·m^{-1} and 1 S·m^{-1}.

3.2 Does the conductivity of the AFM influence the tips performance?

Another interesting issue related the AFM tip is whether its conductivity can influence the resonance behavior of the Ag coating. It is known that commercial silicon AFM tips are often highly doped with boron to disperse the charges which tend to accumulate on the sharp apex. Thus, commercial silicon AFM tips have a much higher conductivity than the case of bulk Si. As the exact value of the optical constant of those highly doped Si tip is not accessible, we assumed a much simpler setting for our model: two Ag-coated dielectric tips with the same dielectric constant 3.48 (this is the value of pure Si in the material library of COMSOL [21]) but different conductivities. The result is shown in Fig. 5. Although the conductivity of the two tips simulated here differ by twelve orders of magnitude, the spectral responses of the field enhancement plots virtually overlap. Therefore, the influence of the conductivity on the LPs resonance is minor.

3.3 Other considerations

To exclude unwanted shape dependencies, we fixed all the geometric parameters of the Ag-coated tip, such as the vertex angle of the tip, the thickness of the coating, the shape of the tip apex, etc. in our simulation. Nevertheless, it is expected that changing these parameters can modify the resonance behavior of Ag-coated tips to some extent. In fact, a similar effect has recently been observed, and is intensively studied in the context of nanoshell structures [25].

Another issue related to the geometry of Ag-coated dielectric tips is the surface roughness of the Ag layer. In practice, the Ag coating is never smooth, and the surface corrugation will surely influence the performance of the tip. One interesting observation in our prior experimental study was that, although the morphology of the Ag layer produced by vapor coating was rather rough and in controllable, the yield of 'hot' tips was high. Therefore, a

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study of how random roughness of the Ag layer influences the resonance could be an interesting future project.

4. Conclusion

We simulated the spectral features of Ag-coated dielectric tips with different optical properties. We found that the frequency, width and magnitude of the plasmon resonances of an Ag-coated tip can be significantly modified by the refractive index of the tip body. Considering all factors that may influence the TERS performance, an AFM tip with a low permittivity provides the best result.

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