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Theoretical study on surface plasmon properties of gold nanostars

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Abstract. With the rapid development of nanotechnology, the surface plasmon properties of metal nanostructures have become the focus of research. In this paper, a multi-tip gold nanostars (GNSs) structure is designed theoretically, and its surface plasmon properties are simulated by using the finite element method (FEM), which is practical and versatile. Compared with the traditional spherical and triangular plate particles, the results show that the tip structure of the GNSs has a stronger hot spots effect, resulting in greater local field enhancement properties. The relationship between the structure parameters of GNSs and their resonance peaks was also studied. The results indicate that the resonance peaks of GNSs depend strongly on the size, spacing between two GNSs, quantity and refractive index of the GNSs.

1. Introduction

Since 1950s, when the Ritchie research group published its research work in the field of surface science [1], people began to have a deeper understanding of the surface plasmon properties. Essentially, the surface plasmon is a collective oscillating state when the incident light interacts with a free electron on a metal surface, due to the same frequency of incident electromagnetic wave and the free electron [2]. A non-radiative local model bound to metal surface. Depending on the nanomaterials, the surface plasmon presents two different forms of expression. One propagates along the interface between the metal and the medium, and the other transforms into a highly localized surface electric field [3,4]. By studying the energy conduction and local field excitation properties of the surface plasmon, many novel optical properties of the surface plasmon have been gradually discovered. Based on these properties, it is possible to regulate the transmission direction, local field intensity, polarization of light and so on, which has important applications such as biology, physics, chemistry, medicine and so on [5-7].

However, the morphology of metal nanomaterials will have a great impact on the surface plasmon resonance absorption properties. The more complex of metal nanostructure, the more it will have a new resonance peak. The maximum field strength is located on the surface of the particle, especially at the tip of the particle, which is called a hot spot [8, 9]. The local field is greatly affected by the complexity of metal nanostructures. The more the tip, the more hot spots, the more sharp the tip, the stronger the hot spots. Hot spots are very important for the application of surface plasmon enhancement effect. In recent years, there have been a lot of preparation and processing techniques of nanomaterials, which can regulate metal nanostructures in nanometer scale to change their influence on optical electromagnetic field. The realization of surface regulation has greatly promoted the development of surface plasmon. At present, the research fields on the surface plasmon properties are gradually rich, such as fluorescence, surface enhancement Raman scatting, solar cells, photocatalysis, nano-lasers, nano-antennas and so on [10-12]. Therefore, it is of great significance to further study the unique optical effects of surface plasmon nanostructures.

2. Results and Discussions

2.1. *Influence of gold nanoparticles on morphology*

At first, the particles of sphere, triangle plate and nanostars were simulated by finite element method (FEM). As shown in figure 1, their surface plamsmon resonance spectra range from 400 to 1200 nm for incident light. It can be found from the figure 1 that when the incident light wavelength is the same as the resonant wavelength of metal nanostructures significant local field enhancement can be obtained. But at the same time, it was found that the position of their resonance peaks was different, and the enhancement effect was also very different. For the multi-tip gold nanostars (GNSs), the maximum electric field enhancement effect is obtained, and the electric field enhancement is more than 300 times at the position of the resonance peak 640 nm, followed by the enhancement effect of the nano-triangular plate and the worst enhancement effect of the nanospheres. Figure 1b-d show the electric field distribution of nanosphere, triangular plates and GNSs, respectively. Therefore, we will focus on the GNSs with the strongest optical resonance effect.

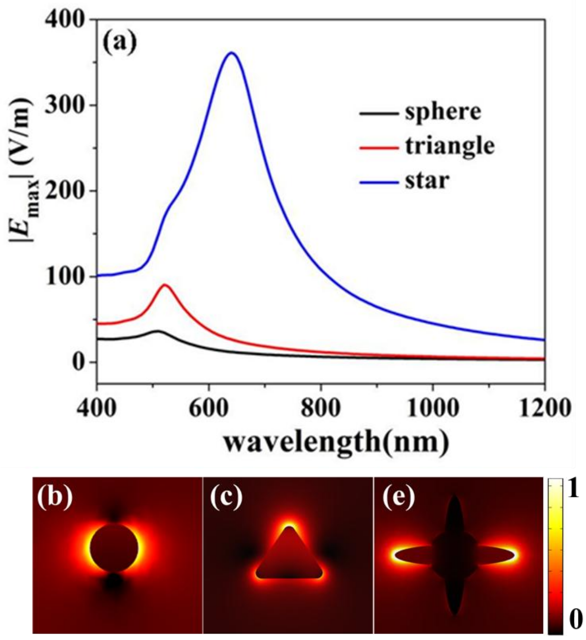

Figure 1. (a) Resonance spectrum of gold nanosphere, nanotriangular plate, GNSs, (b-d) Corresponding electric field distribution map.

2.2. *Influence of GNSs tip size*

The frequency of electron reciprocating vibration in metal nanostructures is determined by the structures size and morphology. Under the condition of resonance, the free electron interaction between light and metal surface is strongest, and the maximum scattering enhancement and local light effect are formed on the surface of metal structure. The 'core' of the center of the GNSs is fixed at R=15 nm. The relationship between the tip size and the resonance peak of the GNSs is studied by changing the size of the tip of the GNSs, as shown in figure 2.

As can be found from figure 2a, as the tip of GNSs becomes longer, the position of the surface Plasmon resonance peak shifts from 580 to 640 nm, and the intensity of the resonance peak increases and the resonance spectrum expands somewhat. The red-shift of the resonance peak is due to the size effect of particles. As the tip becomes longer, the distance between the interfacial charges of the GNSs along the polarization direction of the electric field increases, so the return force, that is, the attraction between the positive and negative charges becomes weaker. As a result, the period of electric dipole oscillation is increased, which results in the decrease of resonance frequency and red-shift of the resonance peak. And the intensity of the resonance peak is due to the lightning rod effect becomes more obvious as the tip becomes longer, and the charge accumulates at the tip with a higher density. Figure 2b shows the electric field distribution of different tip length L of GNSs with incident wavelengths 600 nm.

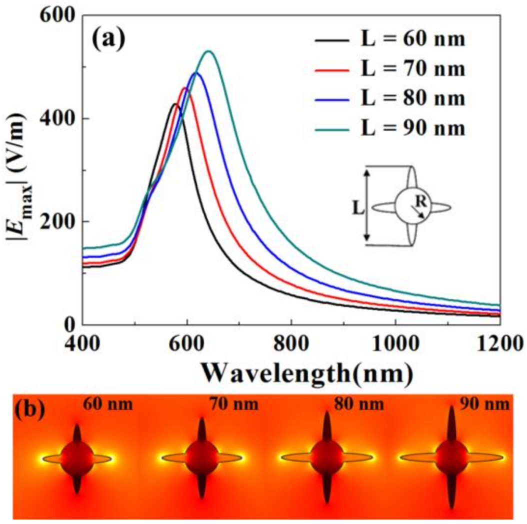

Figure 2. (a) Resonance spectrum of GNSs with different tip length L, (b) Corresponding electric field distribution map.

2.3. *Influence of GNSs distance*

On the basis of a single GNSs model, we further study the influence of the distance between two GNSs models on the local field characteristics. As shown in figure 3, the core in the center of the GNSs R=20 nm, the tip size is 80 nm, and the GNSs distance is 1, 2, 4 and 10 nm, respectively. The refractive index of the surrounding environment is 1, that is, vacuum. Figure 3a shows the surface Plasmon resonance spectrum of GNSs at four distances. Figure 3b displays the corresponding electric field distribution map. The resonance peak of a single GNSs is about 600 nm. When the two GNSs are close to each other, with the decrease of the distance, the resonance peak appears obvious red shift, and the local field intensity increases to 103 orders of magnitude. When the distance between particles decreases 1 nm, the main peak of the resonance peak shifts to 770 nm, and the local field intensity between GNSs reaches 1850, which is much higher than that of single GNSs.

Therefore, by adjusting the GNSs distance, the red shifted to the near infrared band, and the local field intensity can be effectively increased by more than a hundredfold, which can be used in surface enhancement spectrum. When the GNSs distance is 1 nm, the electromagnetic enhancement factor can reach 106 orders of magnitude. If it is used for Raman enhancement, the enhancement factor can reach 1012. Meanwhile, it can be seen that there are two resonance peaks in the resonance spectrum of the two GNSs, in which the larger peak is due to the coupling effect between the GNSs, and the smaller peak is the intrinsic resonance peak of the GNSs itself.

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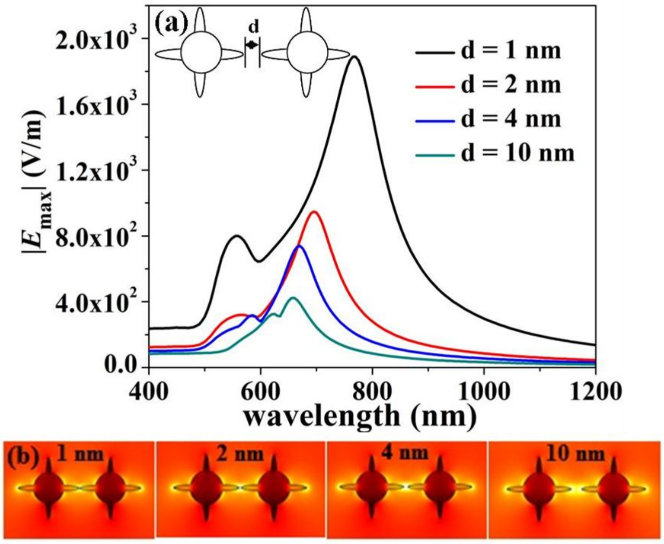

Figure 3. (a) The surface Plasmon resonance spectrum of GNSs at four distances between two GNSs, (b) corresponding electric field distribution map.

2.4. *Influence of GNSs number*

We then regulate the resonance peak by changing the number of particles in the model. As shown in figure 4, the core in the center of the GNSs R=20 nm, the tip size is 80 nm, and the GNSs distance is 0.5 nm. The increase in the number of GNSs will result in the red-shift of the resonance peak, and the maximum resonance intensity of the two GNSs is 8000. As the number of GNSs continues to increase, the resonance intensity decreases. There are also two peaks in the resonance spectrum of several GNSs. The larger peak is due to the coupling effect between the GNSs, and the smaller peak is the intrinsic resonance peak of the GNSs itself.

When the GNSs expands into a chain on a dimension, it will form a dipolar, low-energy horizontal resonance mode while maintaining the original vertical resonance mode. As the shape of the particles becomes more complex, the physical symmetry axis of the particle becomes larger and more undegraded resonance modes appear. Moreover, the optical properties of the particles become more complex, and the superposition of multiple resonant modes covers a wide spectrum range. Figure 4b displays corresponding electric field distribution map of several GNSs.

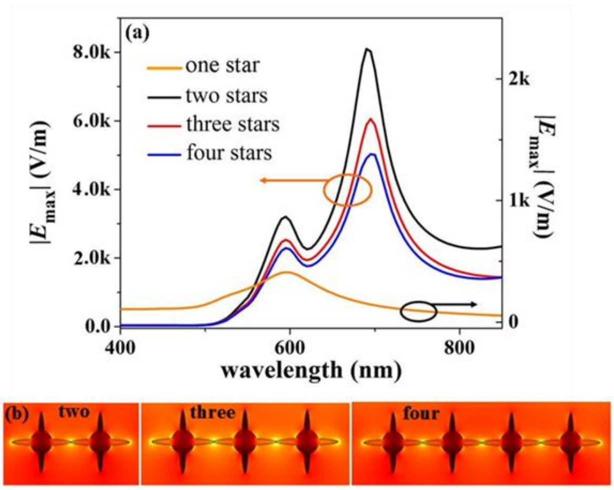

Figure 4. (a) The surface Plasmon resonance spectrum of several GNSs,(b) corresponding electric field distribution map.

2.5. *Influence of surround refractive index*

We also analyze the influence of the dielectric environment around the GNSs on its surface Plasmon resonance characteristics. As illustrated in figure 5, the influence of the surrounding refractive index of 1, 1.2 1.4, 1.6 and 1.8 on the electric field characteristics of GNSs is simulated. The results show that with the increase of refractive index, the resonance peak shifts from 600 to 1000 bands. It shows that the resonance spectrum of GNSs is very sensitive to the dielectric environment around them. At the same time, we find that the resonance spectrum has been widened, and the resonance intensity has not been decreased sharply, and the high electric field intensity has been maintained.

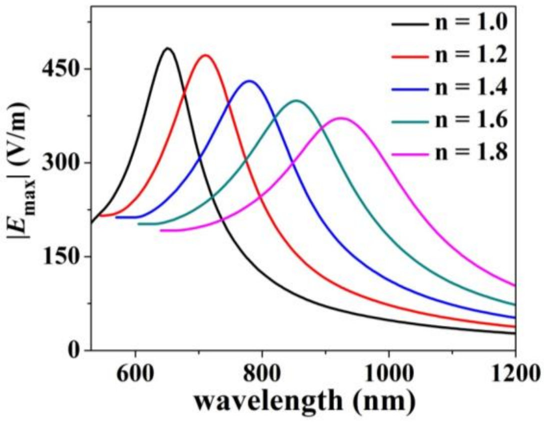

Figure 5. The surface Plasmon resonance spectrum with different surround refractive index.

3. Conclusion

In a word, the simulation result show that the GNSs structure with multi-tip has stronger resonance intensity. Far higher than the ordinary sphere nanostructure. The resonance peak can be regulated by changing the size, distance, quantity and the surrounding refractive index environment of the GNSs. In the case of multiple GNSs, the resonance peak can be regulated to near infrared band. In view of the extremely strong hot spot effect at the tip of the GNSs, it has potential applications in many fields, such as surface-enhanced Raman scattering, surface-enhanced fluorescence and so on.

Acknowledgments

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