Research Article

Size Effects of Closed Encounter Ag Nanoshell Pairs for SERS Application

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Closed encounter Ag nanoshell pairs with remarkable improved plasmonic light enhancement in their gaps have been attracting much attention in the production of sensitivity SERS substrates. This work demonstrates the size effects of Ag nanoshell pairs on obtaining higher light intensity in their gaps. It is found that very complex light intensity changes occur in the gaps of Ag nanoshell pairs with their diameter enlargements (diameters > 100 nm). By the calculation of scattering efficiency and electric field vectors, the size-related light intensity changes in the gaps have been revealed and been concluded systematically. This work fills in the gaps of application of nanoshell pairs with larger sizes in SERS detectors and could guide the design of some other Ag nanoshell pair-based optical devices.

1. Introduction

Noble metallic nanoshells such as Ag and Au have been attracting a lot of attention due to their large tunable plasmonic resonance in the visible spectrum [1–3]. Closed encounter Ag and Au nanoshells (nanoshell pairs) show more significant light enhancements in their gaps and have remarkable improved plasmonic light enhancement [4], which makes them highly attractive as sensitivity SERS substrates, drug deliverer, etc. [5, 6]. Many experimental and theoretical researches have been focusing on the plasmonic resonance of Ag and Au nanoshells with particle diameters smaller than 100 nm which are used as drug deliverer from the medical safety perspective [7, 8]. However, few relevant studies have been undertaken on nanoshell pairs with larger diameters.

As reported, the significant light intensity enhancement in the gaps of nanoshell pairs can be attributed to the highly hybridized plasmon modes [9], which are mainly dependent on their distance, shell thickness, core dielectric functions, and diameters [10]. Among these parameters, size- (shell thickness, diameters) induced plasmonic oscillation order

changes have significant effects on the light intensity in the gaps of nanoshell pairs. Higher plasmon modes excited by nanoshell pairs with diameters larger than 100 nm could cause complex response of light intensity in their gaps [11]. Owing to this, more details of size effects are urgently needed to know the nanoshell pair-based SERS devices' design.

The finite difference time domain (FDTD) method which is based on the Max dimensional equation has been widely used to understand the near-field or far-field light of nanomaterials with complex interfaces by calculating the steady-state continuous wave from the time domain signal [12]. Many studies have proved that the FDTD method is an accurate and timesaving way for obtaining the exact optical response of metallic nanostructures [13, 14]. Therefore, it is adopted herein to reveal the size effects on the light enhancement in the gaps of closed encounter Ag nanoshell pairs. Using FDTD, we found that complex light intensity changes occur in the gaps of Ag nanoshell pairs with the increase in diameters. Through the scattering efficiency and electric field vector calculation, direct relations between the light intensity in the gaps and the plasmonic oscillation have been revealed.

And based on such relations, various-sized Ag nanoshell pairs with high light intensity in their gaps have been selected for the design of SERS devices.

2. Materials and Methods

Generally, low-order oscillation (mainly dipole oscillation) can be supported on Ag nanoparticles and nanoshells with diameter smaller than 100 nm in the visible spectrum, while only beyond this diameter may higher-order oscillation be excited. Herein, Ag nanoshell pairs with overall diameter D ranging from 50 to 200 nm and thickness d varying from 5 to 15 nm have been adopted to study the size effect on the light enhancement in the gaps of Ag nanoshell pairs. The definitions of the diameter D and shell thickness d are presented in Figure 1(a). In our case, the distances between the nanoshell pairs are fixed at a proper value (10 nm) to exhibit clear changes of the light intensity in the gaps. The absorption and scattering properties of these Ag nanoshell pairs are studied by a plane wave light source with a wavelength ranging from 400 to 800 nm based on FDTD calculation. To present the size effect on the oscillations, the electric field vectors of Ag nanoshell pairs with $D = 50, 100, 150$ nm, and 200 nm and $d = 7.5$ nm have also been calculated by the FDTD method.

3. Results and Discussion

Considering the application of Ag nanoshell pairs in SERS detectors [15], we adopted plane wave sources with a wavelength of 532 nm, the most commonly used wavelength in SERS detectors, to study the size effect on the light intensity changes in the gaps of nanoshell pairs. As shown in Figure 2(a), the light intensity in the gaps of Ag nanoshell pairs with diameters of 50 nm and a fixed distance of 10 nm decreased after the thickness was increased from 5 to 15 nm. Nearly contrary changes occur in the gaps of Ag nanoshell pairs with diameters larger than 50 nm with the increase in thickness. As shown in Figures 2(b)–2(d), significant light intensity increase can be observed as their thickness increases, especially for $D = 200$ nm. Ag nanoshell pairs with the greatest thickness obtain the highest light intensity in the gaps, and light enhancement can barely be observed in the gap with a thickness of 5 nm. As a result, the nonlinear relation between the size and the light intensity in their gaps makes it difficult to choose the proper diameters and thickness of Ag nanoshell pairs applied for SERS.

It is known that the scattering/absorption efficiency can directly reflect the plasmonic oscillation excitation of metallic nanostructures [16]. To well know such size-dependent light intensity in the gaps of Ag nanoshell pairs, Figure 3 presents the scattering cross section of Ag nanoshell pairs with D ranging from 50 to 200 nm and d ranging from 5 to 15 nm across the entire visible spectrum. Clear scattering peaks of Ag nanoshell pairs can be observed in Figure 3(a), in which the peak shifts from 405 nm to 540 nm as d decreased from 15 to 5 nm. And slight peak broadening can also be observed. Such phenomenon can be explained by the hybridization theory [17], which states that the hybridization of oscillation of both cavity and nanoparticles causes the bonding ω_+ and

FIGURE 1: Schematic diagram of the nanoshell pairs.

antibonding ω_- hybridized plasmon modes. The detailed explanation can be concluded as

$$\omega_{\pm} = \omega_B^2 \left[0.5 \pm \frac{1}{2(2l+1)} \sqrt{1 + 4l(l+1) \left(\frac{D-2d}{D} \right)^{2l+1}} \right] \quad (l = 1, 2, \dots), \quad (1)$$

where l is the angular quantum number, $\omega_B = \sqrt{4\pi e^2 n_0 / m_e}$ is the intrinsic resonance of Ag, and n_0 and m_e are the free electron density and electron mass, respectively. When d decreases, the bonding plasmon mode ω_+ increases and the antibonding plasmon mode ω_- decreases for a single Ag nanoshell causing the hybridization increase, which generally lead to significant red shifts of oscillation peaks. However, D shows the contrary effects with that of d . When D decreases, the bonding plasmon mode ω_+ decreases and the antibonding plasmon mode ω_- increases for a single Ag nanoshell. When Ag nanoshells combine into pairs, surface coupling in the gaps between nanoshells could lead to further red shift and peak broadening due to the damping effect [18]. Owing to this, the decrease in d of Ag nanoshell pairs with $D = 50$ nm causes significant red shift and peak broadening in Figure 3(a). And the significant light intensity enhancement in the gap of Ag nanoshell pair with $d = 5$ nm in Figure 2(a) can be attributed to such oscillation peak red shift to the wavelength 550 nm, which is quite close to the wavelength of the SERS light source. When D is increased to 100 nm, two oscillation peaks can be clearly observed, as shown in Figure 3(b). Apparently, Ag nanoshell pair with the largest thickness $d = 15$ nm has the oscillation peak closest to 532 nm, which shows significant different tendency from that of Ag nanoshell pair with $D = 50$ nm, which leads to the obvious light intensity enhancement of Ag nanoshell pair as the thickness increase. As shown in Figure 3(c), all of the oscillation peaks are far away from 532 nm, which corresponds to the overall low light intensity with different thicknesses in Figure 2(c). Above all, the nonlinear relation between the size and the light intensity within the gaps of Ag nanoshell pairs can be well explained below: the oscillations peaks of Ag nanoshell pairs (diameter 50 nm) mainly localized to the left side of 532 nm, which is contrary to that of Ag nanoshell pairs (diameters 100 nm and 200 nm). The shell thickness decrease causes the oscillation peak red shift surrounding 532 nm of Ag nanoshell pairs with a diameter of 50 nm. But for Ag nanoshell pairs with larger diameters (100 nm and 200 nm), the shell thickness decrease leads to the oscillation

(a)

(b)

(c)

FIGURE 2: Continued.

FIGURE 2: Light intensity in the gaps of Ag nanoshell pairs with various diameters and thickness: (a–d) Ag nanoshell pairs with diameters 50, 100, 150, and 200 nm and with shell thickness 5, 7.5, 10, and 15 nm.

FIGURE 3: Scattering cross section of Ag nanoshell pairs with various diameters and thickness: (a–d) Ag nanoshell pairs with diameters 50, 100, 150, and 200 nm and with shell thickness 5, 7.5, 10, and 15 nm. Three common wavelengths (532, 633, and 785 nm) of laser sources applied in SERS detectors are marked by dashed lines.

peak red shift far way from 532 nm, which leads to the light intensity decrease within the gaps of Ag nanoshell pairs. In addition, abnormal blue shifts and peak narrowing of Ag nanoshell pairs with $D = 150$ nm and d increase from 7.5 to

15 nm can also be found. However, overall red shifts and peak broadenings can be observed in Figure 3(d) when D increases to 200 nm. Therefore, when selecting the nanoshell pairs with appropriate size, it is necessary to keep them as

FIGURE 4: (a–f) Electric field vector diagram of Ag nanoshell pairs with diameters 50, 100, 150, 200 nm and thicknesses 7.5 nm.

FIGURE 5: Ag nanoshell pairs with proper sizes to obtain significant light enhancements between their gaps: (a) diameter 100 nm, thickness 10 nm by 633 nm light illumination; (b) diameter 100 nm, thickness 5 nm by 785 nm light illumination; (c) diameter 200 nm, thickness 7.5 nm by 633 nm light illumination; (d) diameter 200 nm, thickness 5 nm by 785 nm light illumination.

close to the oscillation peaks as possible. For better choices, three common wavelengths (532, 633, and 785 nm) of laser sources applied in SERS detectors are marked with dashed lines in each figures.

To further understand the size effect on the oscillations in Figure 3, especially for explaining the occurrence of the totally abnormal blue shift and peak narrowing with $D = 150$ and 200 nm in Figures 3(c) and 3(d), typical electric field vector diagrams of Ag nanoshell pairs are presented in Figure 4. Figure 4(a) shows obviously the dipole oscillation excited on Ag nanoshell pairs with $D = 50$ nm, while in Figures 4(b) and 4(c) with $D = 100$ nm, the dipole oscillation corresponds to the 700 nm peak and the quadrupole oscillation corresponds to 475 nm. Apparently, the phenomenon found in Figure 3(c) is not blue shift and peak narrowing of the dipole oscillation peaks. It could be attributed to the asymmetric quadrupole oscillation, which is enhanced around 450 to 580 nm, as shown in Figure 4(d). For Ag nanoshell pairs with a diameter of 200 nm, more complex higher-order oscillation modes are excited, as shown in Figures 4(e) and 4(f). Obviously, these complex order excitations on Ag nanoshell pairs with large diameters lead to the nonlinear light intensity changes in their gaps. However, whether high-order or low-order oscillation, it is the oscillation efficiencies (mainly oscillation peaks) that determine their light intensity in the gaps.

Considering the potential application of Ag nanoshell pairs in SERS, the wavelengths of light sources are fixed at 633 nm and 785 nm [19, 20]. In order to obtain sufficient light intensity, four models of Ag nanoshell pairs with proper sizes have been adopted, as shown in Figure 5. Comparison among these four figures has been conducted, and it was found that nanoshell pairs with $D = 100$ nm and $d = 5$ nm by 785 nm light illumination show the highest light intensity (Figure 5(b)) in the gaps, which should be attributed to the significant oscillation peak around 850 nm. Apparently, the oscillation peak of the Ag nanoshell pair has such size only close to the wavelength of light sources but simultaneously has significant high value. It can be seen clearly that the others which are close to the oscillation peak also have sufficiently high light intensity in their gaps, as shown in Figures 5(a), 5(c) and 5(d). Obviously, the light intensity can be easily tuned to meet SERS detection requirements with various light sources simply by choosing appropriate sizes.

4. Conclusions

In summary, the size effects of Ag nanoshell pairs on their light enhancement between their gaps have been demonstrated by the FDTD method. Firstly, the light intensity in the gaps of Ag nanoshell pairs with various D and d at a wavelength of 532 nm was calculated. Due to the high-order oscillation excited on Ag nanoshell pairs with D larger than 50 nm, complex tendencies of the light intensity changes in the gaps have been observed. Through the calculation of the scattering efficiency and electric field vectors of Ag nanoshell pairs, the relations between the size of Ag nanoshell pairs and the light intensity in their gaps have been concluded systematically. In addition, the size change induced oscillation peak shift and peak broadening/narrowing has

also been presented. Furthermore, by adopting the appropriate sizes, some typical models of Ag nanoshell pairs with high light intensity have also been provided. This work not only offers the theoretical basis for the design of nanoshell-based SERS detectors but could also benefit some other Ag nanoshell pair-based optical devices.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

Authors' Contributions

Zhiguo Zhao and Wenwen Liu contributed equally to this work.

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