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Analysis of Asymmetric Dipoles Interacting in Heterogeneous Metal Nanorod Dimers

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Abstract The localized electric field enhancement of Au-Ag nanorods dimer is theoretically investigated based on finite element method (FEM). An analytical mutual-interference model between asymmetric dipole-dimer has been built to describe the dipoles coupling with different resonance modes in heterogeneous dimer. Three prominent enhancement peaks could be observed from ultraviolet to visible spectrum, in which the ultraviolet resonance especially corresponds to a higher mode in both Ag and Au nanorods. The results reveal the strong coupling mechanism among different dipoles existing in the asymmetric dipole system, which could support the design of plasmonic nanodevices in larger resonance wavelength range.

Keywords Localized surface plasmon resonance (LSPR) · Heterogeneous dimer · Mutual interference · Dipole coupling

Introduction

The optical properties of noble metal nano-structures under visible-light wavelength scales are a subject of both theoretical and experimental interest. The metallic nanostructures has attracted tremendous attentions especially for its prominent near field enhancement effects, which has the potential application in surface-enhanced Raman scattering (SERS), single molecule detecting, biosensor and photothermal therapy [1–6].

Recently, it is observed that the strongly interacting resonances can exist in heterodimers, which have shown advantages over the homodimers in many aspects such as broadening the resonance spectrum or leading to a stronger enhancement in the dimer gap [7–9]. In the narrow gaps of homodimer structures, a strong electric field enhancement can be observed due to the coupling resonance properties [4, 10, 11], which can be theoretically explained by the interaction between a pair of symmetric dipoles [12, 13]. In heterodimers, however, the coupling between two different resonance modes could be even stronger than that in homodimers. Abundant resonance modes can be supported by these symmetry breaking properties of the dimers due to these strong couplings so that higher resonance modes with multi-diploes have been observed in the heterodimers in recent reports [14–16]. In spite of all of these efforts, a systematic study of the optical properties of these heterogeneous nanostructures has not been comprehensively addressed yet. In particular, the effects of mutual-interference in the transition from homo to heterodimers are not completely understood and deserve to be studied more deeply as it may give rise to interactions of different nature, which could be important from both scientific and technological standpoints.

In this article, the near field enhancement effects localized on the gap of Au-Ag heterodimers is numerically investigated by using the finite element method (FEM). An analytical model based on the interference between dipoles in the nanorods with different resonance modes has been used to describe the coupling effect on heterogeneous dimer. We observed the prominent electric field enhancement from ultraviolet to visible spectrum via tuning the distance of the dimer gap. The

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results can be explained by the mutual-interference between heterogeneous dipole-dimer.

The Modeling and Methods

The scheme of the simulation is shown in the top left part of the Fig. 1. The heterodimers consist of a pair of silver and gold nanorods with the same geometry (60 nm in length and 10 nm width). The incident light propagates perpendicular to the nanorod dimer, and the polarization of the light is along the axis of the rods. The refraction index of the noble metal is cited in the ref. [17, 18], and refraction index of surrounding is 1. In order to evaluate the electric field enhancement in the heterogeneous dimer, a mutual-interference model between heterogeneous dipole-dimer has been employed. For an isolated nanorod in the uniform electric field, the polarized dipole in the rod can be described as

$$\mu = \varepsilon_0 \varepsilon_m \alpha(\varepsilon, \omega) E \tag{1}$$

where E is the strength of electric field, ε_m is the electric constant of the medium, and the polarizability $\alpha(\varepsilon,\omega)$ can be described as

$$\alpha(\varepsilon, \omega) = (1+\kappa) V \left(\frac{\varepsilon(\omega) - \varepsilon_m}{\varepsilon(\omega) + \kappa \varepsilon_m} \right) \tag{2}$$

where V is the volume of the nanoparticle, κ is the geometry-dependent factor always larger than 2 [], and $\varepsilon=\varepsilon'+j\cdot\varepsilon''$ is the electric constant of metallic materials. The resonance condition of an isolated nano-particle can be given by $\mathrm{Re}[\varepsilon(\omega)]+\kappa\varepsilon_m=0$. For a heterogeneous dimer system, however, electric field induced by the neighboring dipole must be considered. A universal model describing interference between a pair of dipoles in a heterogeneous system should be shown as ref. [19]:

$$\begin{aligned} \mu_1 &= \varepsilon_0 \varepsilon_m \alpha_1(\varepsilon_1, \omega) \left(E + \frac{\mu_2}{2\pi \varepsilon_0 \varepsilon_m d(d+l)(d+2l)} \right) \\ \mu_2 &= \varepsilon_0 \varepsilon_m \alpha_2(\varepsilon_2, \omega) \left(E + \frac{\mu_1}{2\pi \varepsilon_0 \varepsilon_m d(d+l)(d+2l)} \right) \end{aligned} \tag{3}$$

where d is the gap width between the two rods and l is the length of the rod. By solving the equation set (3), we can get

$$\mu_i\big|_{i,j=1,2} = \varepsilon_0 \varepsilon_m \alpha_i \left(1 + \frac{\alpha_j}{2\pi d(d+l)(d+2l)} \right) E\eta(\alpha_i, \alpha_j) \tag{4}$$

where

$$\eta(\alpha_i, \alpha_j) = \frac{1}{1 - \frac{\alpha_i \cdot \alpha_j}{[2\pi d(d+l)(d+2l)]^2}} \tag{5}$$

In Eq. (4), α_i represents the intrinsic resonance property of the nanorod and $(1+\alpha_j/(2\pi d(d+l)(d+2l)))$ represents the interacting resonance property of another nanorod. So the

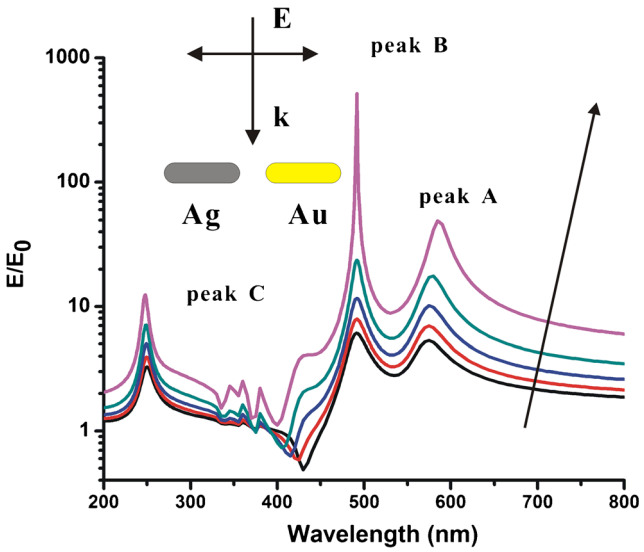

Fig. 1 Near field enhancement spectrum in the middle point with the variation of the distance between Ag-Au nanorod; the *arrow's direction* means gap width decreases from 50 to 10 nm

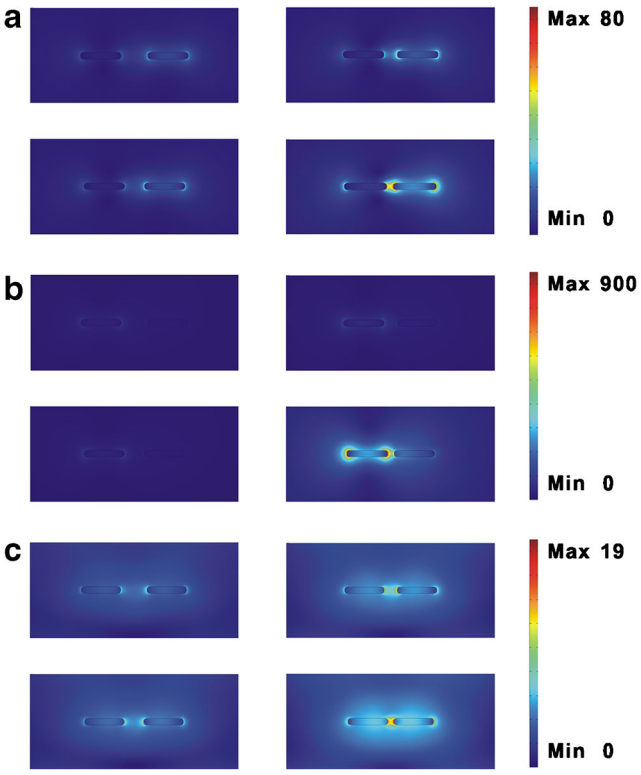

Fig. 2 Electric distribution near the heterodimer at the peak wavelength about **a** 600 nm, peak A,**b** 500 nm, peak B, **c** 250 nm, peak C. The silver rod is on the *left hand* of the dimer picture and the gold one is on the *right*. The gap width in each group of dimer pictures is 40, 30, 20, and 10 nm

electric field around one nanorod could be not only enhanced near the resonance frequency of the rod itself but also enhanced near the resonance frequency of another rod in the heterodimer because of the interference process. With the d decreasing, the interference effect can be more evident. When the intrinsic resonance condition is satisfied, the electric around the rod is stronger than another due to a stronger dipole which can also be seen from the Eq. (4). In addition, the shift of the resonance wavelength in dimer structures could also be explained by the mutual-interference model by revising Eq. (4) as

$$\mu_i\big|_{i,j=1,2} = \varepsilon_0\varepsilon_m(1+\kappa)'V\left(\frac{\varepsilon_i(\omega)-\varepsilon_m}{\varepsilon_i(\omega)+\kappa'\varepsilon_m}\right)\left(1+\frac{\alpha_j}{2\pi d(d+l)(d+2l)}\right)E \tag{6}$$

where

$$\left(\frac{1}{1+\kappa}\right)' = \frac{1}{1+\kappa} - \frac{V\alpha_j}{[2\pi d(d+l)(d+2l)]^2} \tag{7}$$

and

$$\kappa' = \frac{1-\left(\frac{1}{1+\kappa}\right)'}{\left(\frac{1}{1+\kappa}\right)'} = \frac{1-\frac{1}{1+\kappa}+\frac{V\alpha_j}{[2\pi d(d+l)(d+2l)]^2}}{\frac{1}{1+\kappa}-\frac{V\alpha_j}{[2\pi d(d+l)(d+2l)]^2}} \tag{8}$$

When a bonding mode exists, α_j is also a positive factor so κ' is larger than κ. So a new resonance condition, $\mathrm{Re}[\varepsilon(\omega)]+\kappa'\varepsilon_m=0$, should be satisfied, which corresponds to a longer wavelength according to the Drude electron theory or experimental results [17, 18].

Results and Discussion

A full view of the near field enhancement spectrum of Ag-Au nanorod with variable gap widths is shown in Fig. 1. Three obvious peaks at the wavelength of 600, 500, and 250 nm can be observed. The electric field near the inner ends of the rods presents evident enhancement with the decrease of the gap

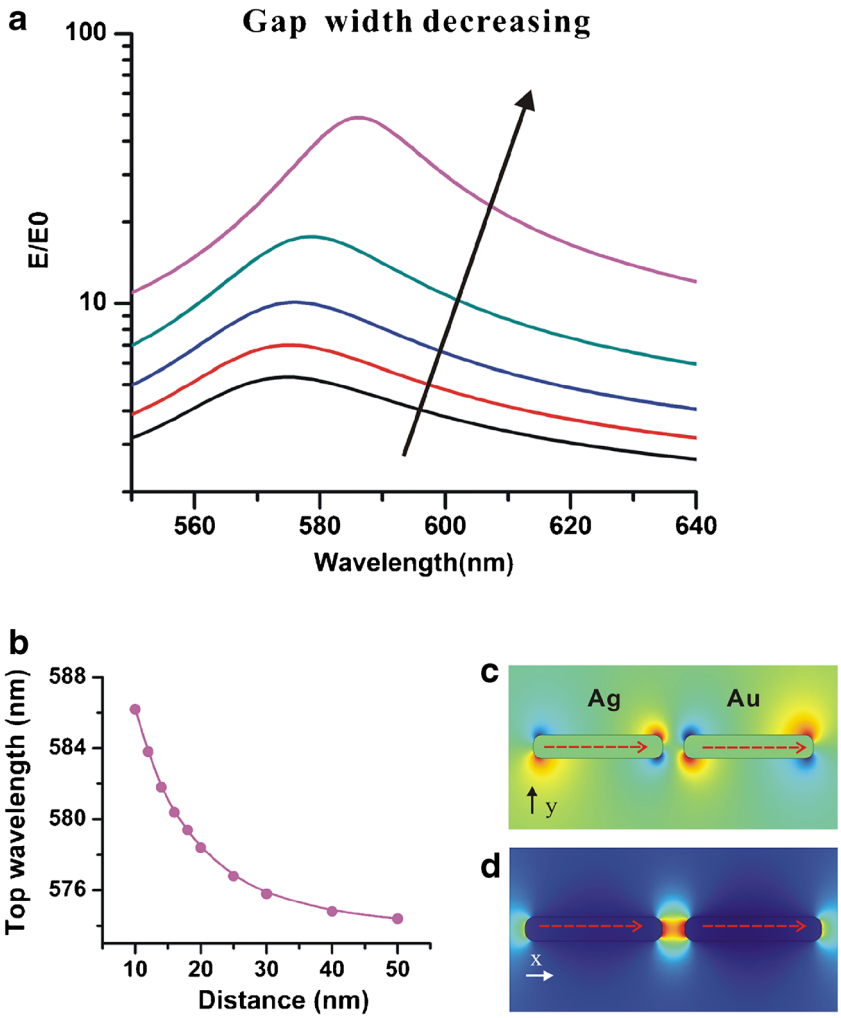

Fig. 3 **a** Detailed near field enhancement spectrum from 545 to 645 nm, the *arrow's direction* means the gap width decreases from 50 nm to 10 nm **b** red-shift curve depending on the width of the gap varying from 50 to 10 nm. **c** Distribution of electric field in *y*-direction. The gap width is about 10 nm. The warmer color means the positive field and the colder color means the negative field. **d** Distribution of electric field in *x*-direction

width. As the gap width decrease, the mutual-interference effect can be even stronger, which has been shown theoretically above.

Variations of the electric field depending on the gap width at the peak A are shown on Fig. 2a. When the two rods get closer from 40 to 10 nm, the electric field around both two rods is strongly enhanced, showing that resonance of the two rods can be strengthened through the mutual-interference effect. In addition, the Au nanorod has a "brighter" resonance than the Ag nanorod, which corresponds to a stronger electric field, indicating that the electric field enhancement at peak A is dominated by the surface plasmon resonance of the Au nanorod and the frequency of the incident light is near the intrinsic resonance frequency of Au nanorod. Near field enhancement happening at peak B can be observed in Fig. 2b. At this peak, when the width d decreases to 10 nm, the electric field strength can be amplified to more than 500 times compared with the incident light. In addition, the electric field around Ag rod is much stronger than that around Au rod. At the peak B, the near electric field distribution indicating that the coupling of the dimer is dominated by the resonance of Ag rod and the resonance of Au rod also has enhancement due to the mutual-interference effect. Another enhancement peak (peak C) exists in the ultraviolet range (with the resonance wavelength about 250 nm) where the enhancement is weaker than peaks A and B. At peak C, evident resonances exist around both Ag and Au nanorods and the electric field in the inner end can be enhanced through the mutual-interference between two multi-dipoles resonance modes. Both Ag and Au nanorods can be excited near the resonance wavelength with higher resonance modes which differs from the base modes existing at peak A and peak B. The detail about these three peaks will be discussed in the following sections.

The near field enhancement spectrum of the resonance dominated by Au nanorod is shown in Fig. 3a. As the width of the gap between the two rods changes from 50 to 10 nm, the exact resonance wavelength of the dimers varies from 575 to 586 nm, indicating that there is observable red-shift when the two rods get closer and interference effect becomes stronger. The red-shifted wavelength depending on the dimer gap width can be clearly shown in the inset, indicating that as the gap width decreases, the red-shift becomes evident. This red-shift can be described as the coupling end-to-end dipoles pairs, forming a bonding plasmon mode, which has been

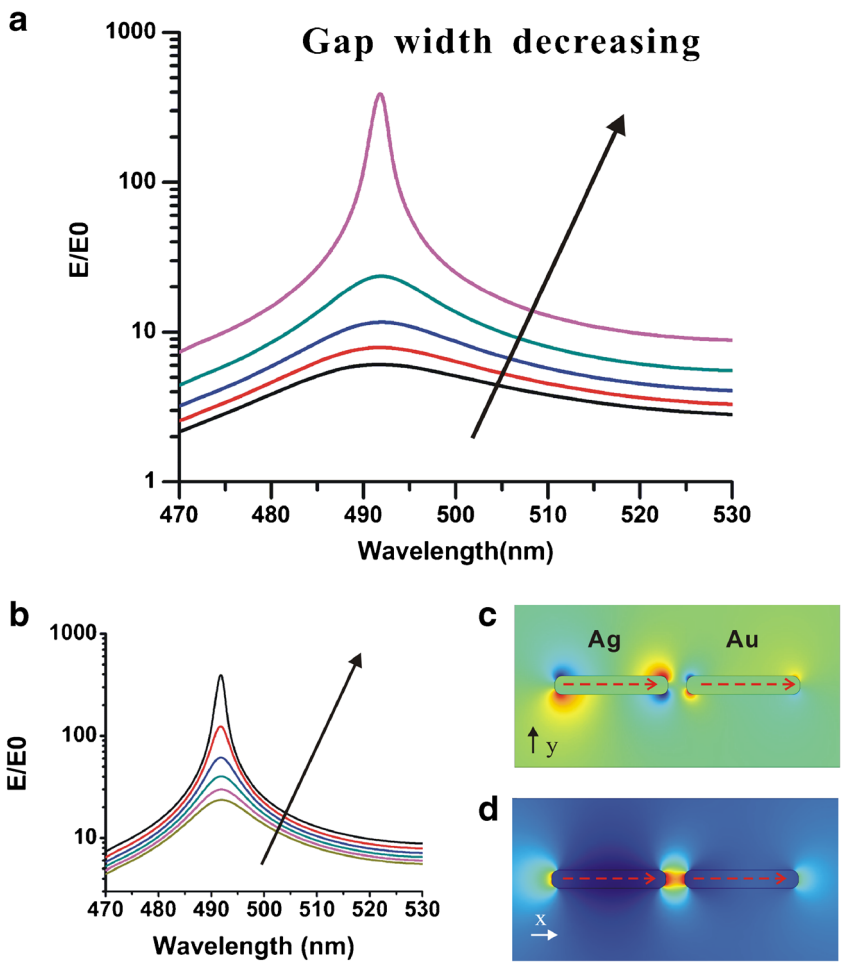

Fig. 4 **a** Detailed electric field enhancement spectrum from 470 to 530 nm, the *arrow's direction* means the gap width decreases from 50 to 10 nm. **b** Detailed enhancement spectrum depending on the width of the gap varying from 20 to 10 nm. **c** Distribution of electric field in y-direction. The gap width is about 10 nm. The warmer color means the positive field and colder means the negative field. **d** Distribution of electric field in *x*-direction

theoretically explained above in Eq. (6). These end-to-end "dipole" bonding mode can be presented in Fig. 3c, d. The electric field distribution on the *y* direction indicates a negative pole at the outer end of the Ag rod. At the inner end closed to the Au rod, the polarity is opposite to the left end, proving that there is a dipole arranged along the axis of the Ag rod from right to left. In the same way, the *y* direction electric field near the Au nanorod can be explained, showing that the dipole direction is the same as the Ag rod. Similarly, the electric field in the *x* direction is shown in Fig. 3d. The electric field direction along the axis of the dimer is always the same, which is just similar to the electric field of two dipoles along the axis. In addition, the electric field near Au rod is stronger than that around Ag rod, which has been explained above in the article.

The enhancement spectrum about peak B is shown in Fig. 4. The near field enhancement spectrum can be seen in Fig. 4a in which exact resonance wavelength is 491 nm. Noticing that the near field is strongly enhanced as the gap width changes from 20 to 10 nm, a detailed enhancement spectrum is shown in Fig. 4b. As the gap width varies from 20 to 12 nm, no prominent enhancement can be observed. When the gap decreases to 10 nm, however, the electric field presents more than five times enhancement. The electric field distribution on *x* and *y* directions are shown in Fig. 4c, d respectively. The directions of the two dipoles are the same, so the coupling between Ag rod and Au rod is also the bonding mode. The electric field around Ag rod is much stronger than that around Au rod, indicating that this strong resonance is dominated by the resonance of Au rod. In addition, the interference effect leads the resonance enhancement of Au rod as well. The plasmon resonance of metal Ag could lead to a stronger enhancement because of its special optical properties, which has been reported in published references [4, 11].

The enhancement spectrum of the higher modes is shown in Fig. 5a. A slight blue-shift from 250 to 244 nm can be observed. The plasmon resonance near peak C is higher mode resonance in nanorods, which is a bright mode with an odd number of dipoles in each rod. This higher mode resonance can be proved through Fig. 5b, c. It can be seen from the electric field distribution that the electric field is not only enhanced near the end of the rods but also near the lateral side. The electric field near the left end of the Au rod indicates a positive pole, on the left part of the lateral side; however, an opposite pole can be observed. The field distribution on the right part is almost anti-symmetry to the left part. This kind of field or pole distribution can be explained by three dipoles along the rod drawn on Fig. 5b. Each of the three dipoles has an opposite direction to the nearby. There are also three dipoles arranged along the axis of the Au rod, two of which are on the negative direction and one of which is on the positive direction. To have a better understanding of the multi-dipole resonance or interaction, the evolution of this higher mode depending on the decreasing gap width is shown in Fig. 5c. When the gap width changes from 50 to 30 nm, a stronger electric field appears on the two ends of the rod, meaning that the dipoles near the ends is stronger than the dipole in the middle. As the gap width continuously decreases, the electric field near the lateral side of the rod increases rapidly and even more stronger than that near the ends. It indicates that the middle dipoles of the rods can be enhanced as the interference between the two rods becomes stronger. The enhanced middle dipoles make the total energy of the system even higher, eventually leading to a blue-shift in the enhancement spectrum

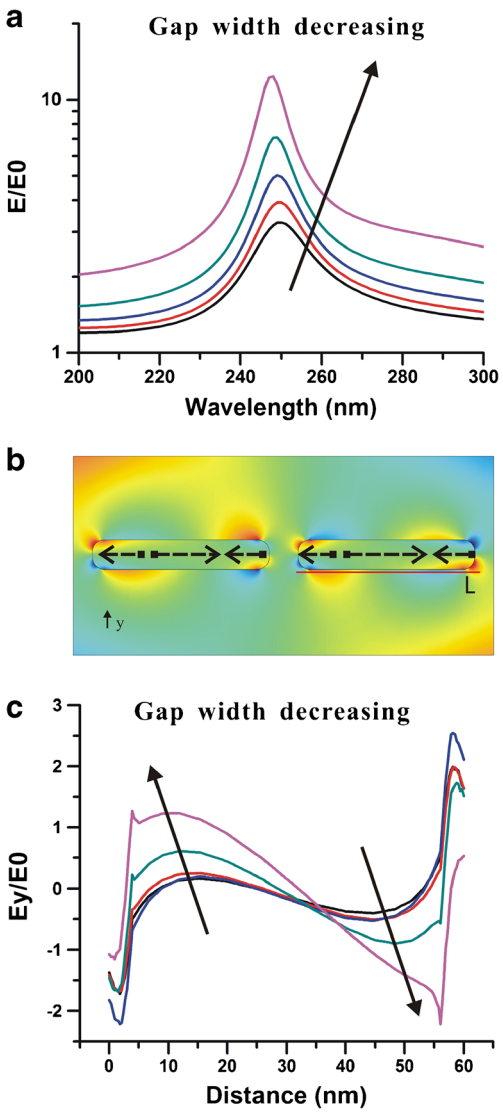

Fig. 5 **a** Detailed enhancement spectrum at peak C from 200 to 300 nm, the *arrow's direction* means the gap width decreases from 50 to 10 nm **b** distribution of electric field in *y*-direction. The gap width is about 10 nm. Each *arrow* in the figure indicates a dipole **c** *y*-direction distribution on the *red line* L in Fig. 5b. The *arrow direction* means the decreasing of the gap width

Conclusion

In conclusion, we theoretically investigated the localized electric field enhancement with Au-Ag nanorods dimer based on the mutual-interacting dipole coupling mechanism. Three prominent enhancement peaks could be observed from ultraviolet to visible spectrum via tuning of distance of the dimer gap, which can be explained by an analytic model based on the mutual-interference between heterogeneous dipole-dimer due to the dimer's different resonance modes. The peak with the largest resonance wavelength corresponds to the resonance dominated by the Au nanorod, at which a clear redshift exists with the gap width decreasing. The peak with a shorter resonance wavelength corresponds to the resonance dominated by the Ag nanorod, where a great enhancement can be observed. The resonance in the ultraviolet spectrum corresponds to a higher resonance mode with multi-dipoles modes in both Ag and Au nanorods. The evolution of this resonance mode with the decreasing gap width is also shown in the article, showing that the middle dipoles of each rod would be stronger as the two rods get closer.

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