The influence of gap spacing in localized surface plasmon resonance (LSPR) spectra of Ag nanorod-coupled with end-to-end assembly using boundary element method

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Abstract. We have systematically investigated the Localized Surface Plasmon Resonance (LSPR) of Ag nanorod-coupled with end-to-end assembly and influence distance between nanorod using metallic nanoparticle based on the boundary element method (MNPBEM). We focused on the extinction curve of LSPR spectra for investigating the effect of gap spacing for this work. It was found that the extinction curve showed two behaviours, for lower wavelength known as the transversal mode and higher wavelength as the longitudinal mode. For further understanding, we also analyzed the electric field related to LSPR spectra of Ag nanorod-coupled. In end-to-end assembly, the resonance peak of transversal mode shifted to lower wavelength (blue-shift) while for longitudinal mode shifted to higher wavelength (red-shift), both as the spacing gap decreased. Interestingly, for the case in parallel polarization, the peaks of wavelength decay as the gap spacing increased followed a plasmon ruler. We observed the dipole-dipole interaction was the influence in LSPR spectra of Ag nanorod-coupled. According to this result, it is essential to understand the distance dependence in LSPR spectra in coupled noble particle system.

Keywords: MNPBEM, Ag nanorod-coupled, end-to-end assembly, LSPR.

1. Introduction

For decades, the investigation on behaviour of Localized Surface Plasmon Resonance (LSPR) spectra of noble nanoparticle (Au and Ag) in array configuration have been intensively studied. The coupling interaction of array configuration has played an essential role in the excitation of the collective electron oscillation on LSPR phenomenon [1] and shows a scaling behavior with an exponential type of LSPR array to the single system [2–5]. However, a few studies have been reported on the influence of gap spacing in LSPR Ag-nanorod-coupled with end-to-end configuration and the threshold value of ratio gap spacing and length of the nanorod.

In this paper, we have observed the influence of gap spacing in LSPR spectra of Ag nanorod-coupled with end-to-end assembly using public optical simulation, metallic nanoparticle boundary element method (MNPBEM). The extinction curve showed LSPR spectra consisted of two peaks. The first peak occurred in lower wavelength was the transverse mode and the second peak in higher wavelength known as longitudinal mode, respectively. The plasmon peaks showed blue-shift in the transverse mode whereas red-shift in the longitudinal mode as the gap spacing decreased. Interestingly, ratio LSPR of Ag nanorod-coupled to single showed a scaling behavior following plasmon ruler with exponential function type. Analyzing the ratio of gap spacing and length of nanorod exhibited a threshold value of LSPR Ag nanorod-coupled acts like single nanorod.
2. Methods

We have investigated the influence of gap spacing in Localized Surface Plasmon Resonance (LSPR) spectra of Ag nanorod-coupled with end-to-end assembly using a public optical simulation metallic nanoparticle boundary element method (MNPBEM) [6] based on boundary element method [7]. From this simulation we obtained the absorption $C_{abs}$, scattering $C_{sca}$, and $C_{ext}$ extinction cross section as the function of wavelength and was written as

$$C_{sca} = n_b \frac{\sum \Re\{\mathbf{n} \times \mathbf{B}^*\}}{4\pi n_b} \frac{1}{\sigma_b}, \quad C_{ext} = -\frac{\sum \Re\{\mathbf{n} \times \mathbf{B}^* + \mathbf{E}_{ext} \times \mathbf{B}\}}{4\pi n_b} \frac{1}{\sigma_b}, \quad C_{abs} = C_{ext} - C_{sca}$$

where $\mathbf{E}$ and $\mathbf{B}$ is the electric and magnetic field vector, $\mathbf{E}^*$ and $\mathbf{B}^*$ is the conjugate of electric and magnetic field vector, and $n_b$ is the refractive index of medium. The diameter was fixed $D = 20$ nm, and the length was $L = 30, 60, \text{ and } 100$ nm or the aspect ratio between the length to the diameter is $1.5, 3, \text{ and } 5$, respectively. The dielectric function of Ag nanorod-coupled used Palik’s experiment [8], and the refractive index medium is $n = 1.3334$. The gap spacing of Ag nanorod-coupled was varied from 5 nm to 500 nm. From this simulation, we produced the extinction curve as the function of wavelength and was presented in figure 2a for the case $D = 20$ nm and $L = 60$ nm or the aspect ratio is 3 and with varying the gap spacing. It was found the extinction curve showed two peaks; firstly, peak occurred in lower wavelength and a second peak in higher wavelength, known as transverse and longitudinal mode, respectively. Further, we observed the peak of LSPR shifted to smaller wavelength as the aspect ratio increased in transverse mode, as shown in figure 2b. It changed around an order of tens. Different in longitudinal, it shifted around the order of hundreds. Its means that varying the aspect ratio will affect the wavelength of LSPR peaks. Increasing the aspect ratio of the nanorod, the plasmon peaks will move to higher wavelength because of the weakening repulsive force between rods. Interestingly in the coupling case, the plasmon peaks tended to shift to higher wavelength in longitudinal while changed to lower wavelength in transverse as the gap spacing decreased. In sense, the transverse and longitudinal mode can be explained by the different polarization that generated the electron oscillation on the surface of nanorod. The electron oscillation occurred along the axis nanorod in longitudinal whereas the short axis of nanorod in transverse.
Figure 2. (a) the extinction curve as the function of wavelength for the case D = 20 nm and L = 60 nm or the aspect ratio is AR=3 corresponds to the gap spacing variation (s = 5-90 nm), (b) the peak of the extinction curve relates to the gap spacing in transverse and longitudinal mode, respectively as the aspect ratio variation.

For understanding, we have also produced the imaging of the electric field intensity of Ag nanorod-coupled for the case aspect ratio AR=3, as presented in figure 3. In the figure, we showed the different LSPR images in transverse and longitudinal modes. The plasmon was formed around the surface of Ag nanorod in transverse while the plasmon occurred at the end of Ag nanorod in longitudinal. Then, these images have also showed the description of LSPR phenomenon in nanorod. For a single Ag nanorod, the radiated electric field caused the charge polarization ±q and the moment dipole was about qL. For the coupling nanorods, the moment dipole was q(2L+s) as the gap spacing changed and became ≈2qL for small the gap spacing.

So, the intensity of Ag nanorod-coupled was higher than single Ag nanorod [9]. The coupling nanorod with end-to-end assembly will excite the opposite surface charges on the end of nanorod in parallel polarization. Then, the attractive forces happened between the nanorod and will reduce the oscillation frequency. Opposite in perpendicular polarization, the nanorod showed the same charge distribution and tended to enhance the repulsive force [10]. This application will increase the resonance frequency and consistent with the extinction curve as explained in figure 2. In simple way, the plasmon resonance of Ag nanorod-coupled can be explained by the dipole-dipole approximation [2].

Furthermore, we have also observed the universal scaling behavior of the extinction peak between Ag nanorod-coupled and single Ag nanorod as a function of the ratio between gap spacing and length of nanorod in longitudinal mode. The peak of plasmon coupling to a single plasmon followed a scaling behavior with exponential decay type to the ratio between the gap spacing and length of nanorod, \( \Delta \lambda / \lambda_o = A \exp(-s/L \tau) \) where \( \Delta \lambda = \lambda - \lambda_o \) where was the difference peak between plasmon coupling to single plasmon, A was a constant value, s was the gap spacing, L was the length of nanorod, and \( \tau \)
Table 1. The exponential fitting value from $\Delta \lambda / \lambda_o$ to $s/L$ for the aspect ratio AR=1.5, 3, and 5

| Aspect ratio (AR) | Constant (A) | Decay length ($\tau$) |
|------------------|--------------|----------------------|
| 1.5              | 0.120        | 0.39                 |
| 3                | 0.145        | 0.26                 |
| 5                | 0.150        | 0.21                 |

Figure 3. The electric field image of Ag nanorod-coupled with end-to-end assembly for (a) transvers and (b) longitudinal mode for the case $D = 20$ nm and $L = 60$ nm or the aspect ratio is $AR = 3$ and $s = 5, 15$ and 30 nm. The colour bar presents the intensity of the electric field.

was the decay length [2]. Figure 4 shows the curve of $\Delta \lambda / \lambda_o$ vs. $s/L$ of Ag nanorod-coupled and the exponential fitting (solid line) for the aspect ratio $AR = 1.5$, 3, and 5. We used the approximation $A \exp (-x/k)$ for exponential function fitting, where $x = s/L$ and $k = \tau$. The fitting results are given in the table 1.
Figure 4. The curve of $\Delta \lambda / \lambda$ vs. $s/L$ and the exponential fitting (solid black line) for the aspect ratio AR=1.5, 3, and 5. The inset figure shows the curve of $\Delta \lambda / \lambda$ vs. $s/L$ in logarithm scale and the value of $s/L$ is denoted by the dot-line.

More interestingly, our data calculation followed a scaling behavior and fitted well with the exponential function, as explained above. From table 1, the aspect ratio increased, the value of $A$ relatively increased, and the decay length tended to decrease. It means, that the parameter of $A$ related to coupling strength that contributed to LSPR peaks shifting and the decay length $\tau$ related reducing the electric field intensity as the gap spacing increased. The determination of $A$ was around 0.12 to 0.15, and the decay length $\tau$ was around 0.21 to 0.4 showed a good agreement with others results [11–14]. Next, we also analyzed the value of $s/L$ for the aspect ratio variation. With changing in logarithm scale, we can determine a threshold value of $s/L$, as presented in the inset of figure 4. The value of $s/L$ was 2.67, 2.17, and 2 for AR = 1.5, 3, and 5, respectively (dot-line). The inset figure of figure 4 describes the threshold value. These results show the LSPR peaks of coupling nanorods act like single nanorods at the particular gap spacing.

4. Conclusions
In summary, we have observed the influence of gap spacing of Ag nanorod-coupled with end-to-end assembly using MNPBEM simulation concerning the aspect ratio and gap spacing variation. LSPR spectra showed two peaks that related to transverse and longitudinal modes as the result of polarization directions of the radiated field according to the short and long axis of nanorods. The LSPR peaks of coupling nanorods shifted to lower wavelength (blue-shift) in transverse mode and higher wavelength (red-shift) in longitudinal as the gap spacing decreased. Also, a dipolar coupling model explains this behavior qualitatively as a result of interference of near field each nanorod. The coupling plasmon peaks respect to single as a function of $s/L$ showed a scaling behavior with exponential function and followed with plasmon ruler behavior. The threshold value of $s/L$ in this work showed behavior LSPR spectra of coupling Ag nanorods were same as single nanorods; it is useful to predict the interparticle gap spacing in the biological system

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References
[1] Jain P K, Eustis S and El-Sayed M A 2006 J. Phys. Chem. B 110 18243–53
[2] Su K H, Wei Q H, Zhang X, Mock J J, Smith D R and Schultz S 2003 Nano Lett. 3 1087–90
[3] Huang C P, Yin X G, Kong L B and Zhu Y Y 2010 J. Phys. Chem. C 114 21123–31
[4] Tabor C, Murali R, Mahmoud M, and El-Sayed M A 2009 J. Phys. Chem. A 113 1946–53
[5] Gunnarsson L, Rindzevicius T, Prikulis J, Kasemo B, Käll M, Zou S and Schatz G C 2005 J. Phys. Chem. B 109 1079–87
[6] Hohenester U and Trügler A 2012 Comput. Phys. Commun. 183 370–81
[7] de Abajo F J G and Howie A 2002 Phys. Rev. B 65 115418
[8] Lynch D W, and Hunter W R 1997 Critiques, metals: an introduction to the data for several metals Handbook of Optical Constants of Solids vol 2, ed E D Palik (London: Academic
Press Ltd) pp 341–409
[9] Aizpurua J, Bryant G W, Richter L J, de Abajo F J G, Kelley B K and Mallouk T 2005 Phys. Rev. B 71 235420
[10] Rechberger W, Hohenau A, Leitner A, Krenn J R, Lamprecht B and Aussenegg F R 2003 Opt. Commun. 220 137–41
[11] Jain P K, Huang W and El-Sayed M A Nano Lett. 7 2080–8
[12] Funston A M, Novo C, Davis T J and Mulvaney P 2009 Nano Lett. 9 1651–8
[13] Jain P K and El-Sayed M A 2010 Chem. Phys. Lett. 487 153–64
[14] Ben X and Park H S 2011 J. Phys. Chem. C 115 15915–26