Investigation the exponential decay of LSPR Ag nanorod-coupled with side by side configuration using boundary element method

Nesy Fitria\textsuperscript{1}, Muhammad Sujak Mansur Kuddah\textsuperscript{1}, Dede Djuhana\textsuperscript{*}
\textsuperscript{1} Department of Physics, FMIPA Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia
dede.djuhana@sci.ui.ac.id

Abstract. In this study, we have systematically investigated LSPR spectra of Ag nanorod-coupled with side of side configuration by a public optical modelling, MNPBEM. The electromagnetic field was applied in perpendicular and parallel direction. The simulation showed the extinction peaks shifted to red-shift in longitudinal mode while shifted to blue-shift in transverse mode as the gap distance increased. The electric field distribution showed increasing in area between nanorod in transverse mode as the gap distance reduced. Contrary, the electric field distribution relatively was constant in longitudinal mode. The electric field increased at end of Ag nanorod-coupled. Furthermore, we have also calculated the different value of Ag coupling and single nanorod to the aspect ratio of the gap distance and the length of nanorod. Interestingly, it was found following the exponential behaviour in longitudinal mode with the decay length related to the electric field distribution as the gap distance increased.

Keywords: LSPR, Plasmon coupling, side by side configuration

1. Introduction
For recent years, the development of nanoparticles research has brought many advantages to various application such as sensor, bioimaging, cancers [1]. Noble particles such as Au, Ag, Cu, and alloys based on noble particle shows a resonance collective conduction electron that known as localized surface plasmon resonance (LSPR) [1,2]. The spectra of LSPR depends on shape, size, composition, medium, and structure [2,3]. One of part LSPR issue relates to the coupling configuration and the gap distance since useful to enhance the sensitivity and intensity of LSPR [2]. Several works have been reported about the coupling configuration in noble particle [4-7]. However, there are few studies about the effect of the gap distance in Ag nanorod-coupled and the decay length of coupling configuration. In this study, we have investigated LSPR of Ag nanorod-coupled with side by side configuration based on optical simulation, Metallic Nano-Particle Boundary Element Method (MNPBEM). The length of nanorod and the gap distance of coupling are varied. The incident wave is applied on Ag nanorod-coupled in perpendicular and parallel polarization. We find the different LSPR spectra Ag nanorod-coupled and single nanorod to the aspect ratio the gap distance and the length of nanorod showed an exponential behavior and followed plasmon rule phenomenon.
2. Simulation method
In this study, we carried out the public of optical modeling MNPBEM to investigate the exponential decay of LSPR Ag nanorod-coupled with side by side configuration based on boundary element method [4,8]. The side by side configuration of Ag nanorod-coupled and the incident wave application were illustrated in Figure 1. The diameter $D$ of Ag nanorod was fixed in 20 nm and the length $L$ was varied from 30 nm, 60 nm, and 100 nm or the ratio of the diameter and length were 1.5, 3, and 5, respectively. The gap distance of Ag nanorod-coupled, $s$ was from 5nm to 210nm. The dielectric function of Ag nanorod was used by Palik’s experiment [5] and the refractive index of medium was water $n_m=1.334$. Then, we applied the incident wave in perpendicular and parallel direction of Ag nanorod configuration to produce the spectra, such as such as absorption, scattering, and extinction cross section as the function of wavelength.

![Figure 1. The configuration of Ag nanorod-coupled with side by side. The diameter D is 20 nm and the length L are 20 nm, 60 nm, and 100 nm. The gap distance of Ag nanorod s is varied from 5 nm to 200 nm. The incident wave is applied in perpendicular and parallel direction.](image1)

3. Results and discussion
The LSPR spectra of Ag nanorod-coupled with side by side configuration for varying the gap distance from 5 nm to 210 nm for the aspect ratio 3 was shown in Figure 2. For this purpose, we only used the extinction cross section as the function of wavelength. There were two mode such as longitudinal and transverse mode, as commonly was found in nanorod shape [1]. The extinction peaks of both longitudinal dan transverse mode shifted as the gap distance changed. The transverse mode shifted to blue-shift while the longitudinal mode shifted to red-shift as the gap distance increased. More, we found LSPR spectra of Ag nanorod-coupled intensity showed higher than LSPR intensity of single nanorod. For the case $s=210$nm, the peak of extinction around $\lambda = 660$nm closed to the peak of single nanorod around $\lambda = 661$nm in longitudinal mode while in transverse mode, the peaks showed same value both Ag nanorod-coupled and single nanorod around $\lambda = 360$nm. Higher LSPR intensity of Ag nanorod-coupled was affected by the surface charge polarization and the dipole moment. Increasing the surface charge of Ag nanorod-coupled caused the LSPR intensity also increased [9,10].
Figure 2. The extinction of Ag nanorod-coupled side by side configuration for s = 5, 15, 30, 120, 180, and 210 nm in the case the aspect ratio is 3 and the single nanorod. The peak of transverse mode is blue-shift and the peak of longitudinal mode is red-shift.

Next, we have also presented the LSPR of Ag nanorod-coupled in the image of electric field distribution for the aspect ratio 3 both transverse and longitudinal mode, as shown in Figure 3. As the figure, we found the coupling interaction was stronger as the gap distance reduced [3]. The value of electric field tended to increase between Ag nanorod-coupled from 6V/m to 12V/m as the gap distance reduced from s = 30nm to s = 5nm in transverse mode. Opposite in longitudinal mode, the value of electric field was not change. The value of electric field showed increasing at end of Ag nanorod-coupled around 30V/m. Based on Figure 3, the coupling interaction of Ag nanorod-coupled was more attractive in transverse mode and tended to blue-shift as the gap distance increased in transverse mode. In longitudinal model, the surface charge at end of Ag nanorod-coupled increased that contributed to the LSPR intensity became higher than single nanorod and tended to red-shift as the gap distance increased.

Further study, we have also investigated the relation of the extinction peak of Ag nanorod-coupled and single nanorod as the aspect ratio between the gap distance and the length of nanorod. It was found the LSPR peak of coupling configuration to a single nanorod followed an exponential decay behavior in longitudinal mode, as reported by Sayed and Huang [6],

$$\Delta \lambda / \lambda_0 = A \exp(-s / L \tau)$$  \hspace{1cm} (1)

where $\Delta \lambda = \lambda - \lambda_0$ was the different the LSPR peak between the coupling and single nanorod. $A$ was constant value, $s$ was the gap distance of coupling, $L$ was the length of nanorod, and $\tau$ was the decay length. The curve of $\Delta \lambda / \lambda_0$ vs. $s / L$ and the exponential fitting for the aspect ratio AR = 1.5, 3, and 5 was presented in Figure 4. For the exponential fitting, we applied the approximation $y = A \exp(-x / k)$ with $x = s / L$ and $k = \tau$. The result of exponential fitting was shown in Table 1.
Figure 3. The electric field distribution of Ag nanorod-coupled in transverse mode (above) and longitudinal mode (below) for the aspect ratio 3 and s = 5nm, 15nm, and 30nm. The bar color presents the ratio of electric field.

Table 1. The result of exponential fitting of $\Delta \lambda / \lambda_0$ vs. $s / L$ for the aspect ratio AR=1.5, 3, and 5.

| Aspect ratio (AR) | Constant (A) | Decay length ($\tau$) |
|------------------|--------------|-----------------------|
| AR = 1.5         | A = 0.14     | $\tau = 0.27$         |
| AR = 3           | A = 0.23     | $\tau = 0.20$         |
| AR = 5           | A = 0.19     | $\tau = 0.10$         |

Figure 4. The curve of $\Delta \lambda / \lambda_0$ vs. $s / L$ and the exponential fitting for the aspect ratio AR = 1.5, 3, and 5 of Ag nanorod-coupled in longitudinal mode.

Based on Table 1 and Figure 4, we showed our calculation following the exponential behavior and fitted to the exponential function. Interestingly, the decay length exhibited decreasing as the aspect ratio increased and the constant A varied around 0.14 to 0.23. The decay length $\tau$ related to the electric
field intensity reduced as the gap spacing increased [7]. The decay length was around 0.10 to 0.27 and the constant $A$ was around 0.14-23 agree with others results [6].

4. Conclusion
In conclusion, we have performed LSPR of Ag nanorod-coupled with side by side configuration. LSPR spectra of Ag nanorod-coupled showed two mode, longitudinal and transverse mode. The peak of LSPR shifted to red-shift in longitudinal mode while blue-shift in transverse mode as the gap distance increased. In longitudinal mode, the different of LSPR peak between the coupling configuration and single nanorod to the ratio between the gap distance and length of nanorod showed an exponential behaviour. The dipole-dipole interaction contributed to enhance the surface charge and increased the LSPR intensity of Ag nanorod-coupled than a single nanorod.

Acknowledgment
The authors would like to thank DRPM Universitas Indonesia for funding this work through Hibah PIT 9 Tahun 2019 under Grant Number: NKB-0023/UN2.R3.1/HKP.05.00/2019.

References
[1] Mahmoud A. Mahmoud and Mostafa A. El-Sayed, “Different Plasmon Sensing Behavior of Silver and Gold Nanorods,” J Phys Chem Lett, vol. 4, pp. 1541–1545, 2013, http://dx.doi.org/10.1021/jz4005015
[2] Kyeong Seok Lee and Mostafa A. El-Sayed, “Gold and Silver Nanoparticles in Sensing and Imaging: Sensitivity of Plasmon Response to Size, Shape, and Metal Composition,” J Phys Chem B, vol. 110, pp. 19220–19225, 2006, http://dx.doi.org/10.1021/jp062536y
[3] B. Lamprecht et al., “Metal Nanoparticle Gratings: Influence of Dipolar Particle Interaction on the Plasmon Resonance,” Phys Rev Lett, vol. 84, no. 20, pp. 4721–4724, 2000, http://dx.doi.org/10.1103/PhysRevLett.84.4721
[4] Ulrich Hohenester, “Simulating electron energy loss spectroscopy with the MNPBEM toolbox,” Comput. Phys. Commun., vol. 185, no. 3, pp. 1177–1187, Mar. 2014, http://dx.doi.org/10.1016/j.cpc.2013.12.010
[5] Edward D. Palik, Handbook of Optical Constants of Solids. Academic Press, 0-12-544420-6
[6] Prashant K. Jain, Wenyu Huang, and Mostafa A. El-Sayed, “On the Universal Scaling Behavior of the Distance Decay of Plasmon Coupling in Metal Nanoparticle Pairs: A Plasmon Ruler Equation,” Nano Lett, vol. 7, no. 7, pp. 2080–2088, Jun. 2007, http://dx.doi.org/10.1021/nl071008a
[7] Srdjan S. Aćimović, Mark P. Kreuzer, María U. González, and Romain Quidant, “Plasmon Near-Field Coupling in Metal Dimers as a Step toward Single-Molecule Sensing,” ACS Nano, vol. 3, no. 5, pp. 1231–1237, Apr. 2009, http://dx.doi.org/10.1021/nn900102j
[8] F. J. García de Abajo, “Retarded field calculation of electron energy loss in inhomogeneous dielectrics,” Phys. Rev. B Vol. 65 115418 http://dx.doi.org/10.1103/PhysRevB.65.115418
[9] J. Aizpurua, Garnett W. Bryant, Lee J. Richter, F. J. García de Abajo, Brian K. Kelley, and T. Mallouk, “Optical properties of coupled metallic nanorods for field-enhanced spectroscopy,” Phys Rev B, vol. 71, no. 23, p. 235420, Jun. 2005, http://dx.doi.org/10.1103/PhysRevB.71.235420
[10] Prashant K. Jain, Susie Eustis, and Mostafa A. El-Sayed, “Plasmon Coupling in Nanorod Assemblies: Optical Absorption, Discrete Dipole Approximation Simulation, and Exciton-Coupling Model,” J Phys Chem B, vol. 110, no. 37, pp. 18243–18253, 2006 http://dx.doi.org/10.1021/jp063879z