Sensitivity of Localized Surface Plasmon Resonance (LSPR) Au Nanorod with Methylene Blue Medium Using Boundary Element Method Simulation

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Abstract. We have calculated the sensitivity of gold nanorod (AuNR) in water solution and methylene-blue based on boundary element method with varying diameter of the nanorod, D are 20 nm, 40 nm, 60nm, and 80 nm. The aspect ratio was varied from 1.5 to 3.5 according to diameter. The dielectric function of AuNR based on Christy and Johnson experiment. To understand the sensitivity sense, we have also varied the medium refractive index is n = 1.3334 (100% water pure) and n = 1.347 (100% methylene-blue pure). The sensitivity of LSPR Au nanorod was determined by the gradient of the peak of wavelength to the refractive index medium variation for all aspect ratio. The LSPR of AuNR consisted of a longitudinal and transversal mode. The longitudinal mode appeared higher wavelength than the transversal mode in LSPR spectra and the peak of wavelength increased as the aspect ratio increased while in transversal mode the peak of wavelength relatively was constant. Furthermore, the sensitivity in longitudinal mode increased as the aspect ratio increased whereas the sensitivity in transversal decreased as the aspect ratio increased. Increasing the sensitivity in longitudinal mode related to red-shift as the nanorod volume increased and the refractive medium index change.

Keywords: Sensitivity, Localized Surface Plasmon, Methylene Blue, The Refractive Medium Index

1. Introduction
The optical characteristic of plasmonic nanoparticles can be adjusted by changing their shape, size, composition of the medium refractive index and structure [1]. Research in the field of nanotechnology shows the results of new products with better performance than large size materials. The LSPR of extinction spectra yielded from accumulated absorption and scattering spectra [2]. The scattering and absorption spectra depend on the shape, size and the refractive index. The ratio of refractive index increases by increasing the particle size such as the variant of diameter [3].
The most applications of noble metal nanoparticles, namely Au, Ag, and Cu referred to the presence of local surface plasmon resonance (LSPR), for instance, biomedical field [4], textile industry [5], energy [6], electronics [7], and agriculture [8]. Currently, many of sensor application use LSPR phenomenon due to their frequency can be tuned by changing of surrounding medium. The important factor to determine the quality of sensor by calculating the sensitivity factor, that is the magnitude of LSPR shift divided the refractive index change. Nanorod sensitivity is a value that represents the ability of nanorods to stimulate the environmental refractive index around nanorod [3]. The sensitivity value is very important especially in nanoparticle applications as sensors. Therefore, knowledge of the sensitivity of Au nanorod is very important in its use as a sensor [9].

In this study aimed calculated the sensitivity of Local Surface Plasmon Resonance (LSPR) phenomenon occurring in Au material from the rod model immersed in two different medium, water and methylene blue and analyzing the LSPR shift pattern from pneumatic on the aspect ratio curve to Au material from the rod model.

2. Simulation Procedure
We have calculated the extinction spectra of Au nanorod using public MNPBEM (Metallic Nano-Particle Boundary Element Method) simulation based on the boundary element method [10]. In this simulation, we varied the aspect ratio from 1.5 to 3.5 with increment 0.5 and the diameter D was 20nm, 40nm, 60nm, and 80nm. The length of Au nanorod followed the aspect ratio, as shown in Figure 1(a). The dielectric function of AuNR was obtained from Johnson and Christy experiment. To calculate the sensitivity, we used two mediums, first the refractive index water $n_w = 1.334$ and methylene blue $n_{mb} = 1.347$. Then, we applied the electric field to Au-nanorod in parallel and perpendicular direction, as presented in Figure 1(b).

![Figure 1](image)

**Figure 1.** (a) Geometry and dimension Au nanorod. The aspect ratio is determined by length and diameter of rod and (b) Polarization direction of electric field.

From this simulation, we generated LSPR spectra such as extinction curve as the function of wavelength. Next, we can determine the sensitivity of Au nanorod with different medium based on the gradient value.

3. Results and discussion
The extinction curve of Au nanorod both water and methylene blue medium as the wavelength were presented in Figure 2. It was observed two modes such as transverse and longitudinal mode, as commonly found in nanorod shape. In the longitudinal mode, the peak of extinction curve shifted to
higher wavelength or red-shift as the aspect ratio increased while the peak slightly shifted to lower wavelength or blue-shift [11].

![Figure 2](image)

**Figure 2.** The extinction of wavelength (a,c) with pure water medium; (b,d) with methylene blue medium by variations of aspect ratio.

The peak of extinction curve happened in visible-near infrared range. To understand, we have also plotted the peak of extinction curve versus the aspect ratio for two medium, as shown in Figure 3. From this figure, we observed shifting the LSPR spectra shift to lower energy in longitudinal mode and higher energy in transverse mode. Interestingly, we have observed the peak of extinction curve moved from visible to near infrared at the aspect ratio around 3 for the case small diameter. On the contrary for large diameter, the peak shifted from visible to near-infrared around the aspect ratio 1.75 [12].

Further, we have also calculated the sensitivity of Au nanorod with two different medium, water, and methylene blue. Figure 4 showed the sensitivity calculation of Au nanorod both longitudinal and transverse mode for the aspect ratio variation. In the case longitudinal mode, the sensitivity value increased as the aspect ratio increased while the sensitivity decreased as the aspect ratio increased in transverse mode. As the figure, we observed the sensitivity of Au nanorod exhibited fluctuation in small diameters such as D = 20nm and D = 40nm. But for large diameters, such as D = 60nm and 80nm was consistently increasing as the aspect ratio increased. Different in transverse mode, the sensitivity decreased following the aspect ratio increased. From this result, it showed the sensitivity of Au nanorod was originated from longitudinal mode where the peak of the extinction curve significantly changed as the aspect ratio increased. Shifting the peak in large diameter was more than small diameter compares to in transverse mode.
**Figure 3.** The LSPR peak of aspect ratio (a) longitudinal mode; (c) transverse mode with pure water medium and (b) longitudinal mode; (d) transverse mode with methylene blue by variations of diameters.

**Figure 4.** Sensitivity of Au nanorod for (a) longitudinal mode and (b) transversal mode.
The result calculated the sensitivity of Au nanorod gave two different polarization. We have also determined the limit range aspect ratio of gold nanorod that occurs in visible range. Then it can be seen the refractive index, diameter, and aspect ratio will produce high sensitivity values for each of the different polarization directions [13].

4. Conclusion
The sensitivity of gold nanorod shaped have been simulated by MNPBEM packaged. The LSPR phenomenon with the nanorod form, namely the transverse mode and the longitudinal mode. It shows, for longitudinal mode the sensitivity with diameter 20nm was 103.40523 RIU/nm, for 40nm was 156.46238 RIU/nm, for 60nm was 228.02452 RIU/nm, and for 80nm was 272.10904. On transverse mode the sensitivity with diameter 20nm was -61.09517 RIU/nm, for 40nm was -75.66319 RIU/nm, for 60nm was -110.62851 RIU/nm, and for 80nm was -112.783012 RIU/nm. The aspect ratio of the length to the variation of diameter affect the shift in resonant wavelength. The variation of environmental refractive index around nanorods also change the peak wavelengths of extinction of Au nanorods. The increasing in environmental refractive index leads to the peak wavelength of the domain with the longitudinal mode of the Au nanorod undergoing a shift to red wavelength (redshift). While the peak wavelength of extinction with the transversal mode of Au nanorod shifts to the blueshift. Sensitivity of the Au nanorod when the variation of the aspect ratio and the environmental refractive index increases, the sensitivity value also changes to greater, and is affected by the increasing diameter for the longitudinal mode.

Acknowledgment
This work was funded by Hibah Publikasi Internasional Terindeks (PIT) 9 Tahun 2019 through DRPM Universitas Indonesia under Grant Number : NKB-0023/UN2.R3.1/HKP.05.00/2019.

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