The sensitivity calculation of localized surface plasmon resonance (LSPR) Au nanorod by applying a boundary element system simulation

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Abstract. In this study, we have calculated the sensitivity of localized surface plasmon resonance (LSPR) Au nanorod by a public metallic particle simulation based on the boundary element method (Metallic Nano-Particle Boundary Element Method, MNPBEM). The diameter of nanorod D is 20 nm, 60 nm, and 80 nm. The variation of aspect ratio is 1.5 to 3.5. The dielectric of Au nanorod based on the Christine-Johnson experiment. To understand sensitivity sense, we have also varied the refractive index medium by Lorentz-Lorentz approximation from a mixture of water and glycerol concentration. The refractive medium index is n = 1.3334 (100 % water pure), n = 1.3605 (80 % water and 20 % glycerol), n = 1.3881 (60 % water and 40 % glycerol), n = 1.4164 (40 % water and 60 % glycerol), and n = 1.4452 (20 % water and 80 % glycerol). From MNPBEM simulation, we have produced LSPR spectra such as absorption, scattering, and extinction curve as the function of wavelength. Then, the sensitivity of LSPR Au nanorod is determined by the gradient of the peak of wavelength to the refractive index medium variation for all aspect ratio. Interestingly, we have found the LSPR Au nanorod consisted of longitudinal and transversal mode in LSPR Au nanorod curve. The longitudinal mode appeared a higher wavelength than the transversal mode in LSPR spectra. In longitudinal mode, the peak of wavelength increased as the aspect ratio increased (red-shift) while in transversal mode, the peak of wavelength was relatively 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. According to the results, the sensitivity determination is useful to understand the refractive index medium changes that it is important to design a sensor device.

Keywords: LSPR, au nanorods, boundary element method simulation

1. Introduction

Nowadays, nanoparticles become one of the topics of interest for researchers to develop science and technology, because nanoparticles are quite important topics in both the scientific and application sides. Nano-scale materials can improve the physical, mechanical, and chemical properties of a material without damaging its atomic structure. Nanoparticles can be applied in various aspects of the biomedical field [1], textile industry [2], energy [3], electronics [4] and agriculture [5]. Research in the field of nanotechnology shows the results of new products with better performance than the large size materials.

Utilization of nanoparticles involves a material surface, where nanoparticles have high reactivity,
Study the sensitivity for different diameter 20 nm for gold used and glycerol (where the medium refractive index is determined by the length and diameter of the nanorod. (a) The aspect ratio is determined by the ratio of length to diameter and (b) Polarization direction of the electric field. Because atoms have a great opportunity to interact, this evidence is found in the development of nanoparticles of gold or Au material. The selection of a gold material is due to its stable properties in the air and water without undergoing oxidation unlike iron or other metals [6]. The SPR redshift is related to the enhancement of the Au NP extinction cross-section since LSPR increases with a wavelength in the 500–700 nm range [7] and the shape of the nanorod influences how light is absorbed [8]. Nanorod sensitivity is a value that represents the ability of nanorods to stimulate the environmental refractive index around nanorod [9]. 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 [10].

This study aims to observe the Local Surface Plasmon Resonance (LSPR) phenomenon occurring in Au material from the rod model, analyzing the LSPR shift pattern from pneumatic on the ratio aspect ratio curve to Au material from the rod model, determining the aspect ratio in the LSPR in the visible light region due to gold material which only looks visible, observing the effect of the medium on the material sensitivity of the LSPR phenomenon.

2. Simulation procedure
This study was performed the sensitivity calculation of single gold nanorod using MNPBEM simulation based on boundary element method approximation. Single gold nanorod with various aspect ratios was used and embedded in a different medium. Then, we scaled up the value of each aspect ratio within three different sizes. First, the small diameter was 20 nm for length (30, 35, 40, 45, 50, 55, 60, 65, and 70) nm, respectively. Second, intermediate diameter was 60 nm for the length (90, 105, 120, 135, 150, 165, 180, 195, and 210) nm, respectively. Third, the larger diameter was 80 nm for the length (120, 140, 160, 180, 200, 220, 240, 260, and 280) nm, respectively. The geometry of nanorod is shown in figure 1a with length (L) and diameter (D). Then, the electric field is given by two different polarizations, which are parallel and perpendicular to long axis as shown in figure 1b. To calculate the medium refractive index, we have applied the Lorentz-Lorentz approximation by equation (1):

\[
\frac{n_{12}^2 - 1}{n_{12}^2 + 2} = \frac{n_1^2 - 1}{n_1^2 + 2} \phi_1 + \frac{n_2^2 - 1}{n_2^2 + 2} \phi_2
\]

where \( n_{12} \) is the refractive index of mixed solution, \( n_1 \) and \( n_2 \) are the refractive index of water (1.33) and glycerol (1.47), and \( \phi_1 \) and \( \phi_2 \) are volume fractions of water and glycerol, respectively. We used the volume fractions for water (\( \phi_2 = 0 \% \)), 80 \% (\( \phi_2 = 20 \% \)), 60 \% (\( \phi_2 = 40 \% \)), 40 \% (\( \phi_2 = 60 \% \)), 20 \% (\( \phi_2 = 80 \% \)), and 0 \% (\( \phi_2 = 0 \% \)), respectively. The dielectric function of gold used the data from Johnson and Christy’s experiment. Then, we analysed the extinction spectra to study the sensitivity for different diameter 20 nm, 60 nm, and 80 nm both longitudinal mode and transverse mode, respectively.

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

Figure 2 shows the resonance peak position in a various aspect ratio of both longitudinal (figure 2a) and transverse mode (figure 2b) against the refractive index changes in diameter 20 nm, 60 nm, and 80 nm, respectively. We found the refractive index change affected the resonance peak position and this result agreed with previous work both theoretically [11] and experimentally [1]. Increasing the refractive index, however, the resonance peak of both transversal mode (TM) and longitudinal mode (LM) shift to longer wavelength [12]. The resonance peak of TM in whole diameter and aspect ratio occurs in visible range as the refractive index increases, but for LM, there is a limit range aspect ratio which is the whole peak resonance occurs in visible range, diameter 20 nm for range 1.5–2.7, diameter 60 nm for range 1.5–2.0, and diameter 80 nm for range 1.5–1.7.

Furthermore, for a given refractive index, we found the resonance peak in each diameter of LM shift to longer wavelength as the aspect ratio increased whereas it was vice versa for the TM. The peak position of TM for a small and intermediate diameter was difficult to be distinguished, while in larger diameter the peak resonance of both TM and LM can be seen. The gradient of linear fit can determine the sensitivity of gold nanorod.

In figure 3, we plotted the sensitivity for different diameter of both longitudinal mode and transverse mode, respectively. The sensitivity was calculated by the wavelength peak displacement per unit changes of medium refractive index \( S=\Delta \lambda_{\text{peak}}/\Delta n \) [1], this is very important for an application like sensor. We have calculated the sensitivity of gold nanorod, in LM for diameter 20 nm was 150.31 RIU/nm, for 60 nm was 218.2 RIU/nm, and for 80 nm was 224.97 RIU/nm. In TM for diameter 20 nm was -52 RIU/nm, for 60 nm was -14 RIU/nm, and for 80 nm was -2 RIU/nm. Interestingly, increasing the diameter affected in the increase of the sensitivity of both longitudinal and transverse mode while aspect ratio just affected in increasing the longitudinal mode sensitivity while the transverse mode tended to decrease [9]. The highest sensitivity of longitudinal and transverse mode was observed in diameter 80 nm. The result show that TM is less sensitive to the aspect ratio changes than LM. The refractive index of LSPRs is wavelength dependent, that is the refractive index will not depend on the mode resonance of the geometry structure once the sensing wavelength is fixed with theoretical results by quasi-static approximation [13].
4. Conclusions
In conclusion, we have successfully calculated the sensitivity of Au nanorod with two different polarizations. The result shows, for longitudinal mode the sensitivity with diameter 20 nm was 150.31 RIU/nm, for 60 nm was 218.2 RIU/nm, and for 80 nm was 224.97 RIU/nm. For transverse mode, the sensitivity with diameter 20 nm was -52 RIU/nm, for 60 nm was -14 RIU/nm, and for 80 nm was -2 RIU/nm. We have also determined the limit range aspect ratio of gold nanorod that occurs in visible range. In transverse mode, for aspect ratio 1.5–3.5 with diameter 20 nm, 60 nm, and 80 nm occurs in visible range. In longitudinal mode, diameter 20 nm for range 1.5–2.7, diameter 60 nm for range 1.5–2.0 and diameter 80 nm for range 1.5–1.7 while the transverse mode occurs in visible range for the whole given aspect ratio. The higher sensitivity was observed for longitudinal mode and transverse mode with diameter 80 nm, respectively.

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