The incident electrical field angle effect in localized surface plasmon resonance (LSPR) of bimetallic Ag-Au nanorod using MNPBEM simulation

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Abstract. In this study, we have performed the incident electrical field angle effect in localized surface plasmon resonance (LSPR) spectra of bimetallic Ag–Au nanorod using Metallic Nano-Particle Boundary Element Method (MNPBEM) based on the boundary element method. The diameter and length of nanorod are 40 nm and 100 nm, respectively. The fraction of Ag in bimetallic Ag-Au are 0, 20, 40, 60, 80, and 100 within weight percent. The dielectric function of Ag–Au was generated by linear approximation and the incident angle used from 0 to 90 degrees. We found that the intensity of the extinction curve shows decreasing follow logistic type curve as the incident angle increases whereas the resonance peak is constant. For a given silver fraction in bimetallic Ag-Au, the resonance peak of LSPR shifted to higher energy or blue-shift and the intensity increased. Interestingly, the LSPR of bimetallic Ag–Au occurred in the visible range and the transition mode from longitudinal to transverse mode was observed at the angle greater than 60 degrees.

Keywords: MNPBEM, alloy gold-silver, nanoparticle, localized surface plasmon resonance

1. Introduction

In the last two-decades, noble nanoparticles, such as Au and Ag had been attracting both in fundamental and application. The development of technology contributes to the noble nanoparticle applications, such as drug delivery, cancer detection and cancer therapy, and tissue imaging was found in the medical area [1–3], biological imaging [4], hydrogen sensor [5,6] and enhanced Surface-Enhanced Raman Spectroscopy (SERS) signal [7,8]. These applications used an excitation property phenomenon of noble nanoparticles known as localized surface plasmon resonance (LSPR), which depend on size, shape, medium, structure, material selected and polarization [7,9,10]. Besides the pure Au and Ag, alloying them have also attracted many researchers both experimentally [4,8,11] and theoretically, such as Discrete Dipole Approximation (DDA) [9,11,12]. Finite Difference Time Domain (FDTD) [5], and Time-Dependent Density Functional Theory (TDDFT) [1]. Silver has higher intensity and resonance energy than gold but easier to oxidize. So, alloying gold with silver is promising to get alloy with good intensity, energy and stability. However, few studies have discussed the electrical field angle effect in LSPR spectra in bimetallic Ag–Au as the composition variation [12].
In this study, we have observed the electrical field angle effect in LSPR spectra of bimetallic Ag–Au nanorod using optical simulation, Metallic Nano-Particle Boundary Element Method (MNPBEM) with various compositions. The angle was given from 0 to 90° and the dielectric function of Ag–Au was generated by linear approximation. We analysed the LSPR spectra both the peak of resonance and intensity. The intensity decreased as the incident angle increased and the peak of resonance shifted to blue-shift as the fraction of Ag increased.

2. Methods
We have performed the angle effect in LSPR spectra of bimetallic Ag–Au nanorod using MNPBEM [13] based on the boundary element method [14]. A full Maxwell approximation was used to produce the LSPR spectra, such as the extinction cross-section. Single bimetallic nanorod Au$_{x}$Ag$_{1-x}$, which are corresponded to the value of x = 0, 20, 40, 60, 80 and 100 within weight percent [10,15] embedded in air with refractive index, n=1.0 [12]. The diameter and length of nanorod are 40 nm and 100 nm, respectively. The dielectric of bimetallic Ag–Au nanorod was generated by linear approximation [16] and the dielectric function of pure Au and Ag were used from the Johnson and Christy experiment [17]. Then, we applied the electromagnetic wave in the z-direction with the angle variation from 0 to 90° with an increment 10 degree, as illustrated in figure 1.

3. Results and discussion
The extinction curve as the wavelength function of bimetallic Ag–Au nanorod for the fraction and the incident angle variation is presented in figure 2. The result of the Au and Ag curve shows two things. First, the intensity of the longitudinal and transverse mode strongly depends on the incident angle. Second, the resonance peak of wavelength is less sensitive with the incident angle. These results agreed with Tuersun’s work by Discrete Dipole Approximation (DDA) simulation [12]. The peak of the extinction curve of bimetallic Ag–Au happened in the visible range and shifted to lower wavelength (blue-shift) as Ag fraction increased [3,16,18]. Shifting to blue-shift of the peak is related to the imaginary part of the dielectric function where the dielectric of Au greater than Ag in visible range [17,18].

Looking detailed in the inset of figure 2, we have observed two peaks happened at a certain incident angle then became a single peak as the fraction of Ag increased. For each composition, two peaks occurred at different angles, for instance, Au pure at an angle 60°, Au$_5$Ag$_{95}$ at 70°, and Au$_{10}$Ag$_{90}$ at 80°. On the other hand, it was not observed for Au$_{50}$Ag$_{50}$, Au$_{70}$Ag$_{30}$, and Ag pure. Changing of two peaks to one peak is related to the direction of the incident light from parallel (0°) to perpendicular (90°) or longitudinal mode to transverse mode.

For understanding, we have also plotted the maximum intensity of extinction as the incident angle (figure 3a) for various compositions. The maximum intensity of extinction decreased following a logistic curve type as the incident angle increased. This result is similar to Fu et al. work with DDA simulations [19]. Interestingly, we found that the intensity of extinction was a little increased for a fraction of Ag less than 40 weight percent whereas for larger than 40 weight percent the intensity of extinction significantly increased. This result was consistent with the previous explanation about the imaginary part of dielectric function of Ag. Increasing of Ag fraction contributed to the increasing the intensity of extinction. In figure 3b, we have also presented the peak of Ag–Au as the incident angle for composition variation. The peak showed a constant value as the incident angle increased [12] and

![Figure 1](image-url)
Figure 2. The extinction curve as the function of the wavelength of Ag-Au bimetallic nanorod to the incident angle and composition Ag-Au nanorod variation. The inset figure shows changing the LSPR spectra from two peaks to one peak due to increasing of the Ag fraction, such as Au\textsubscript{80}Ag\textsubscript{20} and Au\textsubscript{60}Ag\textsubscript{40}.

Figure 3. (a) The peak value of the intensity and (b) the LSPR wavelength as the function of the incident angle in the composition Ag-Au nanorod variation.
shifted to blue-shift as the fraction of Ag increased [16]. More interestingly, we observed the peak of bimetallic Ag-Au slightly shifted for the incident angle around 70º and 80º. This means that we can observe a transition state from longitudinal to transverse mode in bimetallic Ag–Au around 70º and 80º. The peak of transverse mode resonance of bimetallic Ag–Au, however, falls below visible range. Our results showed that the angle effect affected to the LSPR spectra of bimetallic Ag-Au nanorod especially the intensity and a transition from longitudinal to transverse mode.

4. Conclusions
In conclusion, we have observed the effect of angle in LSPR spectra of bimetallic Ag-Au nanorod using MNPBEM simulation. The result showed that the intensity of LSPR spectra decreased as the incident angle increased while the peak of LSPR spectra was relatively constant as shown in figure 3. Increasing of Ag fraction in bimetallic Ag-Au nanorod showed the peak of LSPR shifting to blue-shift and increasing the intensity. Interestingly, the LSPR spectra happened in visible range. We have also observed a transition mode from longitudinal to transverse mode in changing the incident angle direction in the visible light range. The peak resonance for pure Au are 508 nm (transverse mode) and 593 nm (longitudinal mode) happen at 60º, Au, are 497 nm (transverse mode) and 579 nm (longitudinal mode) at 70º, Au, are 496 nm (transverse mode) and 560 nm (longitudinal mode) at 80º while Au’s fraction of more than 60, just one peak appears as longitudinal mode.

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