A numerical study of the sensitivity of surface plasmon resonance bimetallic silver-gold alloys using boundary element method

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Abstract. In this study, we have systematically investigated the sensitivity of surface plasmon resonance bimetallic silver-gold alloys by means of metallic nanoparticle simulation, MNPBEM with respect to the diameter, mole fraction, and refractive index medium variation. The sensitivity of surface plasmon resonance was obtained from a fitting linear between the value of the peak position LSPR spectra and the refractive index medium. Interestingly, it was found the sensitivity of surface plasmon resonance increased as the diameter increased for a diameter less than 40 nm, whereas the sensitivity of surface plasmon resonance exhibited the fluctuation values for diameter above 40 nm. The highest value of the sensitivity occurred at the silver mole fraction at x = 0.6 rather than at x = 1.0 (pure silver particle). This result also showed the sensitivity of surface plasmon resonance pure silver particle (x = 1) was greater than gold particle (x = 0). The sensitivity of surface plasmon resonance was not only affected by the diameter but also influenced by the mole fraction.

1. Introduction

Metallic and bimetallic noble nanoparticle have been attracted much attention due to their potential application for sensing such as biosensor, biochemical sensing, biomedical application, etc. [1, 2]. They produce unique optical properties from the interaction between free electron conduction in noble metallic with the electromagnetic field that known as localized surface plasmon resonance (LSPR). Furthermore, LSPR spectra depends on the size, shape, medium, and configuration [3, 4]. Understanding LSPR spectra includes shifting of the peak position and dielectric sensitivity is very important for designing sensor device based on surface plasmon behavior [5]. Several observations have been reported for the peak LSPR shifting and the sensitivity of surface plasmon resonance, both experimental [6, 7] and simulation [8-10]. However, few observations reported about LSPR shifting such as amplitude and peak position spectra and the sensitivity of surface plasmon resonance bimetallic silver-gold alloy as the diameter, mole fraction, and medium variation.

In this study, we calculated the sensitivity of surface plasmon resonance bimetallic silver-gold alloys with the variation of the silver mole fraction, diameter, and the refractive index medium. We produced LSPR spectra bimetallic silver-gold alloy using a public metallic nanoparticle simulation based on boundary element method. We have observed two behaviors of the LSPR spectra of the silver-gold alloys such as amplitude and the peak position. The LSPR spectra showed shifting to a higher wavelength (red-shift) as the diameter of alloys increased. Interestingly, as the mole fraction of silver increased, the amplitude increased and the peak position shifted to a smaller wavelength (blue-shift).

Then, we calculated the sensitivity of surface plasmon resonance based on the peak position of the LSPR spectra with respect to the refractive index medium and diameter variation.
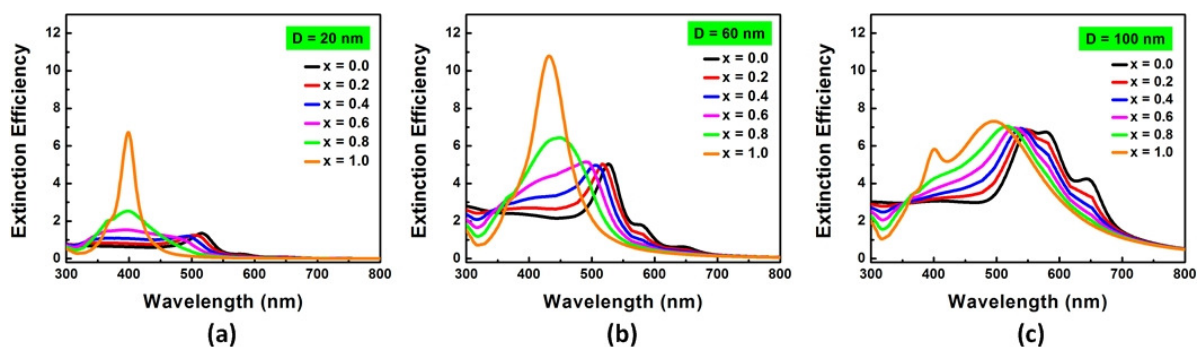
2. Simulation procedure

We have systematically performed the sensitivity of surface plasmon resonance bimetallic silver-gold alloys by means of a public metallic nanoparticle simulation, MNPBEM based on boundary element method [11]. Bimetallica silver-gold alloys (Ag_xAu_{1-x}) was modeled as a spherical particle with the diameter variation from 10 nm to 100 nm. The mole fraction x was varied from 0 to 1 with 0.2 increment. We have also prepared the variation of the refractive index medium to observe the sensitivity of surface plasmon resonance. In this study, we varied the refractive index medium by mixture of water and glycerol concentration based on Lorentz-Lorentz approximation [12, 13], 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). The dielectric bimetallic silver-gold alloys were calculated based on the dielectric silver and gold combination with respect to the mole fraction variation [9, 14]. This simulation produced the LSPR spectra such as extinction, absorption, and scattering curve with respect to the wavelength. We only focused on the extinction curve as representative of LSPR behavior in this study.
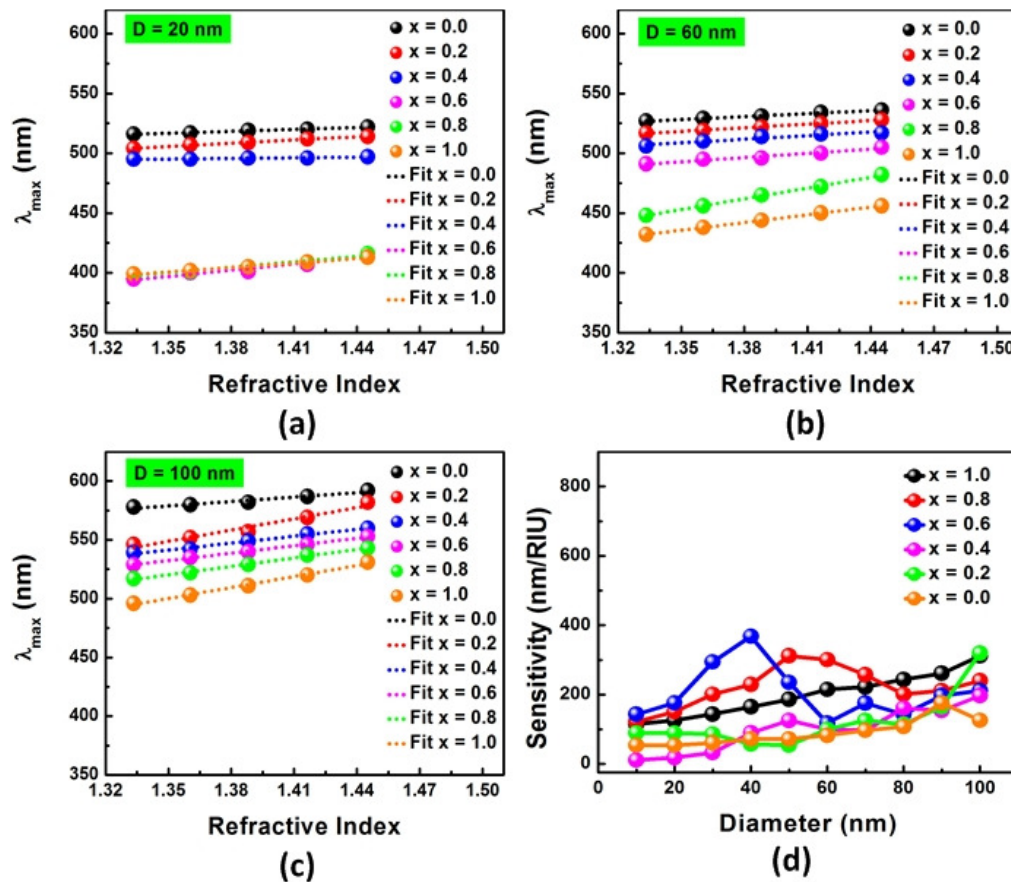
3. Results and discussion

Figure 1 shows the extinction curve of the silver-gold alloys for the diameter and the mole fraction variation under the refractive index medium water n = 1.3334. For understanding, we showed the extinction curve for small (D = 20 nm), intermediate (D = 60 nm), and large diameter (D = 100 nm). Interestingly, the peak position of the extinction curve shifted to a higher wavelength (red-shift) as the diameter of alloys increased and also occurred in the visible light range. The red-shift phenomenon originated from the bimetallic particle interacted with the electromagnetic field that depended on the material, size, shape, and local dielectric properties. The scattering exhibited to be more dominant than the absorption as the particle size increased and the peak position of the LSPR spectra will shift to a higher wavelength [15, 4]. Further, we found two behaviors of the extinction curve such as amplitude and the peak position. As the silver mole fraction increased, we observed the amplitude also increased and the peak position shifted to a lower wavelength (blue-shift). Similar observations have been reported [16, 8].

Interestingly, the extinction curve bimetallic silver-gold alloys exhibited different behavior compared to the extinction curve from pure silver and pure gold particle. Introducing a hybrid surface plasmon resonance from bimetallic particle that originated from d-band and conduction band. We observed, for small and intermediate diameter, the amplitude of the extinction curve slowly increased until the silver mole fraction at x = 0.6, whereas greater than x = 0.6, the amplitude clearly changed. For the case the mole fraction x = 0 and x = 1 related to LSPR spectra pure gold and silver particles, respectively.

Figure 1. The extinction curve bimetallic silver-gold alloys for the mole fraction variation from x = 0 to x = 1 (a) D = 20 nm, (b) D = 60 nm, and (c) D = 100 nm.

Figure 2. The peak position with respect to the refractive index medium variation and the mole fraction (a) D = 20 nm, (b) D = 60 nm, and (c) 100 nm as represented in dot symbol and the dot-line represents the linear fitting. (d) The sensitivity of surface plasmon resonance relates to the diameter bimetallic silver-gold alloys and the mole fraction

Next, we have also produced the extinction curve of the silver-gold alloys corresponded to the refractive index medium variation. Figure 2 exhibits the peak position of the extinction curve for small (D = 20 nm), intermediate (D = 60 nm), and large diameter (D = 100 nm) as the mole fraction and the refractive index medium variation. According the figure, we have found that the peak position still occurred in the visible light range as changing the refractive index medium. The peak position also shifted to red-shift as the refractive index medium increased and blue-shift as the silver mole fraction increased. The values of the peak position from the extinction curve exhibited a linear-like peak position. For small diameter (D = 20 nm), the peak position slowly decreased until the silver mole fraction at x = 0.4 and relatively same value for x greater than 0.4. We have observed there was a large difference value between x = 0.4 and 0.6, such as a transition. In contrast to intermediate and large diameter, the value of peak position decreased as the silver mole fraction increased. Based on Kuzma's work, shifting of the peak position in bimetallic the silver-gold alloys originated from the dipole term rather than interparticle coupling [8].

Furthermore, we calculated the sensitivity of surface plasmon resonance bimetallic silver-gold alloys using a linear fitting based on the peak position and the refractive index medium relation. The fitting results are shown in figure 2a for D = 20 nm, figure 2b for D = 60 nm, and figure 2c for D = 100 nm (denoted in dotted lines). The slope value of the linear fitting was a value of the sensitivity of surface plasmon resonance bimetallic silver-gold alloys [5, 17]. Figure 2d shows the sensitivity of surface plasmon resonance corresponded to the diameter and the mole fraction variation. We observed, for diameter less than D = 40 nm the sensitivity tended to increase as the diameter increased. Above the

diameter 40 nm, the sensitivity exhibited the fluctuation value that depended on the changing of the mole fraction. Interestingly, the highest sensitivity of bimetallic silver-gold alloys occurred in the silver mole fraction at x = 0.6 rather than x = 1.0 at the diameter D = 40 nm. This figure also shows the sensitivity of surface plasmon resonance the silver particle (x = 1.0) was higher than gold particle (x = 0) for all range the diameter. In other words, the sensitivity of surface plasmon resonance the bimetallic silver-gold alloys exhibited to be more stable at the mole fraction x = 0.6 at small diameter. From this result, we suggested to consider the mole fraction when preparing the bimetallic nanoparticle.

4. Conclusions

In conclusion, we have calculated the sensitivity of surface plasmon resonance bimetallic silver-gold alloy with respect to the diameter, mole fraction, and refractive index medium variation. The value of the sensitivity was obtained by a linear fitting based on the peak position and the refractive index medium relation. The sensitivity tended to increase as the diameter increase to 40 nm. Above the diameter 40 nm the sensitivity showed the fluctuation values depended on the changing of the mole fraction. The highest sensitivity occurred in the mole fraction of silver at x = 0.6 at the diameter 40 nm. Beside the diameter, the mole fraction should be considered for observing the LSPR spectra in bimetallic nanoparticle.

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