The localized surface plasmon resonance on noble metal-semiconductor: Au nanosphere-ZnO nanorod

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Abstract. In this work, we have investigated the localized surface plasmon resonance of metal-semiconductor model. The raw materials are gold nanosphere (Au-NP) and ZnO nanorod (ZnO-NR). The nanoparticles were surrounded by air with refractive index constant (1.0+0i). Moreover, the diameter and aspect ratio of Au-NP and ZnO-NR were 40 nm and 4, respectively. Then, we designed the nanoparticle in two different configurations. First, Au-NP was placed at the sides of ZnO-NR and second, Au-NP was placed at the tip of nanorod. Next, we varied the gap-distance among them from 0 nm to 40 nm with 10 nm increment. The photon wavelength used were from 300 nm to 1200 nm within two different excitations (transverse and longitudinal excitation). Furthermore, our result suggests that on the longitudinal excitation, when the gap-distance increases, the resonance peak of second configuration remains at constant value and the intensity significantly decreases compared to the first configuration. However, on the transverse excitation, the first configuration has a high intensity and the resonance peaks is slightly red-shifted. In addition, based on the near-field mapping which reflects the energy density of electromagnetic field by LSPR, the LSPR of Au-NP stands to aid the exciton production to enhance the photocatalytic activity.

Keywords: Surface plasmon resonance, ZnO, gold, photocatalysis activity

1. Introduction
The strong interaction between light and noble metals (e.g. gold, silver, and copper) on the nanoscale display extraordinary applications including bio-sensor [1], enhance-Raman scattering [2], solar cell application [3] and enhance photocatalytic activity [4-6]. The interaction light with metal has been understood in terms of Localized Surface Plasmon Resonance (LSPR), where light energy is trapped in a small length/volume/area without propagation [7]. Furthermore, the utility of LSPR effect was well-known to enhance the photocatalytic activity in semiconductor materials such as ZnO and TiO$_2$ [4, 5, 8]. Noble metals greatly aid to enhance the photocatalytic activity. As reported by Fauziyah et al. in order to increase the efficiency of photocatalytic activity in the case of ZnO, it could be done not only by increasing the surface area, but also the surface active site [8]. In addition, Chou and co-worker reported the sensitivity of Au modified ZnO on different refractive index medium, and showed that the resonance peak shifted to a lower energy as the refractive index increased [9]. Another noble metals such as silver (Ag) had been carried out by Ren and co-worker to modify the ZnO nanorod array for photocatalytic application [10]. Moreover, there were systematical studies about the effect of
electromagnetic coupling between exciton from ZnO and plasmon resonance from gold nanoparticle [11].

However, there was a lack of understanding on how the LSPR affects the photocatalytic activity process. In this work, we have systematically studied by the means of numerical calculation of how the LSPR effect from Au can enhance the spectral of ZnO and we also serve a near-field map of Au nanoparticle adjacent to ZnO nanorod with different gap-distances.

2. Simulation procedure
We have carried out the extinction cross section calculation by employing a metal-semiconductor model, as illustrated in figure 1. The calculation was used MNPBEM Toolbox embedded in MatLab software [12]. This toolbox was utilized a Boundary Element Method approach to build a convenience metal-semiconductor structure. Furthermore, the substraction of scattering cross section and absorption cross section leaves extinction cross section, thus it could be utilized to analyze the result and the electric field map to show the electric responses of Au-NP and ZnO-NR for different gap-distance.

Gold nanosphere with diameter \( D \) 40 nm was employed as well as ZnO nanorod profile with length \( L \) and width \( w \) are 280 nm and 70 nm, respectively or the aspect ratio is 4. These sizes were determined by TEM images as reference [6]. The dielectric function of gold was taken from Johnson and Christy [13] and for ZnO adopted by Stelling’s data [14]. The refractive index of medium around metal-semiconductor is air (1+0i). Moreover, the long-axis of ZnO was situated in line with y-axis (see figure 1) while Au-NP positions were put next to the length and width of ZnO. Then, the gap position \( s \) was determined from the tip of ZnO and Au by varying \( s \) from 0 nm to 40 nm with 10 nm increment. The photon wavelength in range 300 nm to 1200 nm was applied within two difference polarizations, along z-axis and y-axis.

3. Results and discussion
We examined the spectral, namely, Longitudinal Plasmon (LP) mode and Transverse Plasmon (TP) mode. The LP occurred when the electrical part of photon wavelength is polarized along z-axis while TP can be exhibited when the electrical part is properly arranged to be polarized in y-axis (see the inset figure 1). Figure 2 shows the extinction spectra of metal-semiconductor model where Au-NP is situated next to the short-axis of ZnO-NR by gap distance \( s \). It can be observed that, the extinction peak of ZnO is appeared around \( \sim 350 \text{ nm} (\sim 3.5 \text{ eV}) \) due to the UV-light energy absorption that imposes the photocatalytic activity [8, 15]. According to Fauziyah et al. and Musa et al. work, the absorption in the UV region correlates with ZnO band gap energy profile, around \( \sim 3.24 \text{ eV} \) (380 nm) and 3.378 eV (367 nm), respectively. Our simulation was noticeably different from their work in some aspects. It might be come from the dielectric function measurement treatment, meshing of metal-semiconductor model, and environment of metal-semiconductor. Since Au-NP was examined on the center within short gap-distance from nanorod, then a broad band arose around 500 nm to 550 nm. This peak is distinctly the Au-NP itself by comparing to the pure-gold spectra, indicating by dash-line. Increasing the gap distance between ZnO and gold does not affect the LP spectral significantly, both the intensity and LSPRs peak. On the other hand, the TP spectra lead to decrease their intensity as the gap distance increases and LSPRs peak position are slightly blue-shifted as the gap increases from 0 nm (\( \lambda_{LSPR} = 515 \text{ nm} \)) to 20 nm (\( \lambda_{LSPR} = 510 \text{ nm} \)). Then, if the gap distance is much greater than 20 nm the LSPRs peak remains stable at 509 nm.

Figure 3 presents the extinction spectra of ZnO-NR and Au-NP along z-axis as shown in the inset figure. In can be seen that both LP and TP could enhance the ZnO intensities when Au-NP is put at the tip of nanorod. The LP spectra shows that increasing the gap-distance between endcap of nanorod and Au-NP significantly decreases the intensity whilst the LSPRs peak unchanged at 514 nm. However, in TP spectra, it seems that the gap-distance increases to 40 nm, so both intensity and LSPRs peak constantly stands at around \( \sim 2 \times 10^3 \text{ nm}^2 \) and \( \sim 507 \text{ nm} \), respectively. Interestingly, the LSPRs peak of
LP is red-shifted or lowering their energy compared to Au-NP’s peak (~508 nm), but TP’s LSPR no change was observed.

**Figure 1.** The schematic diagram representation of ZnO-NR with Au-NP on (a) side mode and (b) head mode. Gold’s diameter ($D$) is 40 nm, gap between them ($s$) is 0 nm to 40 nm with increment 10 nm, and length ($L$) and width ($w$) of ZnO-NR are 280 nm and 70 nm, respectively.

**Figure 2.** The extinction spectra of ZnO-NR coupled with Au-NP situated perpendicularly to long-axis of nanorod in Longitudinal Plasmon (LP) mode (left) and Transverse Plasmon (TP) mode (right).

**Figure 3.** The extinction spectra of ZnO-NR coupled with Au-NP situated next to long-axis of nanorod in Longitudinal Plasmon (LP) mode (left) and Transverse Plasmon (TP) mode (right).
Figure 4. Near-field map of metal-semiconductor modeled by Au-NP (a) at side of ZnO-NR and (b) upper side of ZnO-NR, within two excitation modes: Longitudinal Plasmon (LP) mode (upper row) and Transverse Plasmon (TP) mode (lower row).

Next, we examined the near-field map distribution of metal-semiconductor model, as shown in figure 4. The configuration of Au-NP at the tip of ZnO-NR (LP mode) was the highest energy electromagnetic (EM) density with photon energy around 2.41 eV (~514 nm). However, on TP mode where Au-NP put at the sides of ZnO exhibiting a strong EM energy density with photon energy 2.40 eV (~515 nm). High EM energy density is due to the confinement in a small region between Au-NP and ZnO-NR when their position are in line with electric part polarization. Furthermore, the confinement of local electric field surround the noble metal (Au) and semiconductor (ZnO) can effectively enhance the photocatalytic activity of ZnO to hinder the electron-hole pair recombination [16]. In this case, the LSPR effect from Au can support and enhance near electromagnetic field intensity to increase the photoreaction [17]. In other word, the LSPR from gold can aid to produce more exciton inside TiO2 to compensate for the loss electron trap effect due to SiO2 insulation [17].

4. Conclusion
In conclusion, we have systematically observed the LSPR phenomena of metal-semiconductor model. The results show that the spectral of ZnO-NR raises when Au-NP is placed on the near surface of ZnO. According to electric field map, the LSPR effect from Au-NP effectively enhances both spectral and electromagnetic energy intensity due to the confinement of strong electric field for the given polarizations.
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