The Thickness Effect on LSPR Spectra of Au-Nanorod Coated TiO$_2$ and SiO$_2$ Studied by MNPBEM

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Abstract. We have studied the effect on localized surface plasmon resonance (LSPR) of Au-nanorod (AuNR) coated TiO$_2$ (Au@TiO$_2$) and SiO$_2$ (Au@SiO$_2$). The length and diameter of AuNR are 70 nm and 20 nm, respectively. For this purpose, then AuNR was coated by TiO$_2$ and SiO$_2$ with thickness varying from 2nm to 20nm with increment 2nm. The LSPR exhibited two modes, transverse mode (TM) and longitudinal mode (LM) as commonly was found in a rod-shaped particle. Interestingly, the peak of extinction red-shift as the thickness increased both TM and LM. Increasing volume and refractive index around AuNR contributed to red-shift, therefore the rate of decreasing energy TiO$_2$ faster than SiO$_2$. Furthermore, we have also observed the peak of LSPR extinction curve of Au@TiO$_2$ have a similar trend to Au@SiO$_2$ as the thickness increased, but its beginning to decrease at ~8nm. In the LM, for a given thickness, we found the peak of extinction curve Au@TiO$_2$ show more than one peak present around ~2-3nm and ~8nm. However, only one peak happened in Au@SiO$_2$. In a sense, Au coated TiO$_2$ can be fully utilized to enhance photocatalytic activity under visible light of AuNR and useful in photocatalytic activity, on the other hand, SiO$_2$ plays an insignificant role for a certain limit thickness under visible light – near-infrared.

Keywords: MNPBEM, LSPR, refractive index, longitudinal mode, transverse mode

1. Introduction

In the recent decade, the inquiry of noble metals such as Au, Ag, and Cu has a gorgeous thought controlled the electron oscillate driven by electric field so-called localized surface plasmon resonance (LSPR). This phenomenon strongly depends on how to controlled the size, shape, morphology, and material used [1] and occurred with prerequisite is the metal size smaller than photon wavelength [2]. The noble metallic was attracting to study because of their unique properties and great potential to applied in technology and shows fascinating surface plasmon in visible range, then mostly used as sensor [3,4], biological imaging [3], catalysis/photocatalysis [5,6], and drug delivery [5]. Its has been well-known coating surrounding the Au-nanorod (AuNR) will influence the LSPR effect. Isabel et al. did gold nanosphere and nanorod shape coated SiO$_2$ and both showed the optical spectra shift to a longer wavelength from visible to near-infrared [7]. Also Wiebke et al. showed gold nanorod coated SiO$_2$ more stable than uncoated [5]. The silica has several advantages as a material veneer to enhance
the thermal, mechanical, and colloidal stability [5]. The AuNR coated SiO$_2$ are good material core-shell structure for sensing application, photoacoustic imaging, and increased the efficiency of the drug delivery process. On the other side, gold coated TiO$_2$ is essential to deeper investigation cause titania is a common photocatalyst [8-10], abundant in the earth [11], non-toxicity [8,11], friendly surrounding, chemical inertness [8], preserve aggregation of metal nanoparticles and low cost. The titania was found in 1969 as a fascinating material for photochemical and photocatalysis application due to TiO$_2$ has a greater band gap (>3.0eV) and was found in three phase such as anatase, rutile, and brookite [12,13]. Rutile is more stable in bulk material and anatase are good water adsorption and has a longer electron-hole pairs lifetime for a surface reaction. For photocatalysis application under visible light is still poor to utilized due to the exciton generated by visible light lower than its band gap, therefore the electron-hole pair recombined rapidly and and no affect photocatalysis [8,10]. The researcher has done many ways to fully utilized titania for photocatalysis. The common ways are doping or coating with a metal or nonmetal [9]. This modification aims to modify the hot electron injection from metal to the conduction band of TiO$_2$ and also the local electric field of incident wavelength can be fully utilized the photocatalysis efficiency enhancement [8], this electron which is initiated by decay surface plasmon resonance [10,11,14].

The main objective of this study, firstly, is determined qualitatively how the LSPR spectra of extinction spectrum AuNR affected by the TiO$_2$ and SiO$_2$ coating, respectively. The TiO$_2$ was used within anatase phase which is as good water adsorption. Secondly, calculated the tunability of maximum thickness AuNR coated TiO$_2$ and SiO$_2$ under visible light – near-infrared (NIR).

2. Simulation procedure

The systematic investigation of thickness effect on LSPR spectra of Au-nanorod coated TiO$_2$ and SiO$_2$ was performed by MNPBEM (Metallic Nano-Particle Boundary Element Method) public software [15] based on boundary element method [16]. The geometry of Au-nanorod (AuNR) with coating TiO$_2$ and SiO$_2$ were presented in Figure 1. The length ($L$) and diameter ($D$) of AuNR are 70nm and 20nm, respectively or the aspect ratio was 3.5. The thickness ($t$) of TiO$_2$ and SiO$_2$ were varied from 2nm to 20nm with increment 2nm. The dielectric function of AuNR was obtained from Johnson and Christy experiment [17]. The refractive index of TiO$_2$ based on Bodurov’s work [18] and SiO$_2$ was adopted Gao’s experiment [19]. For calibrating, we used the Sellmeier equation to recalculate the refractive index of TiO$_2$ in the range 0.251μm-1.5μm.

\[ n^2(\lambda) = 1 + \frac{B\lambda^2}{\lambda^2 - C} \]  

(1)

where $n$ is a refractive index, $\lambda$ is a wavelength in μm, and coefficient B=4.6796 and C = 0.040086. The nanoparticle immersed in water with refractive index $n = 1.33$. Then, we applied the plane wave in parallel and perpendicular to long axis of AuNR with respect to the wavelength 400nm to 1100nm. From this simulation, we produced spectra such as extinction spectrum as the wavelength function and near-field map.

![Figure 1](image)

**Figure 1.** The schematic diagram of (a) AuNR@TiO$_2$ and (b) AuNR@SiO$_2$. 


3. Results and discussion

The LSPR spectra of AuNR pure and coated TiO$_2$ and SiO$_2$ for the thickness variation in the extinction curve, as shown in Figure 2. It was found two resonance modes such as transverse and longitudinal modes, as usually happened in rod shape [1,3,20]. For the case longitudinal modes, the LSPR spectra shifted to longer wavelength or red-shift as the thickness increased both AuNR coated TiO$_2$ and SiO$_2$. The LSPR spectra shifting observed in the range visible-NIR, as shown as in Figure 2(a)-right and Figure 2(b)-right. For transverse mode case, the spectral slowly shifted to red-shift as the thickness increased and all LSPR shifting still occurred in visible range, as depicted in Figure 2(a)-left and Figure 2(b)-left. Further, we have also observed the extinction curve of AuNR coated TiO$_2$ in longitudinal mode around 500nm-700 nm. It was observed that some multiple peaks were formed with low amplitude. For the thickness around 2nm–6nm as labeled (i), it was originated from the interband transition from 5d electron to conduction band excited by the wavelength 550nm-600nm (2.25-2.07 eV) [21], thus this peak also correlated with the peak in transverse mode greater 600nm. This result similar to Winsemius’s work that Au has a limit absorption around ~640nm (~1.94eV) called interband transition [21]. Then, above the thickness 6 nm, others peak began to form in LSPR spectra. This peak was a higher order in LSPR spectra of AuNR such as quadrupole and hexapole mode as indicated (ii).
Figure 2. The extinction spectrum vs wavelength as thickness variation of (a) AuNR coated TiO$_2$ in transverse mode (TM) and longitudinal mode (LM) (b) AuNR coated SiO$_2$ in transverse mode (TM) and longitudinal mode (LM). In inset figure which (i) and (ii) are interband transition and higher order like quadrupole/hexapole mode, respectively.

Next, we have also plotted the peak value of the extinction curve of AuNR related to the thickness variation extract from the longitudinal mode, as shown as in Figure 3. As Figure 3, the peak value of AuNR coated TiO$_2$ was higher than coated SiO$_2$. It was understood the peak value of AuNR coated TiO$_2$ higher than SiO$_2$ since the refractive index of TiO$_2$ larger than SiO$_2$. Large shifting the LSPR spectra of AuNR coated TiO$_2$ widely used in photocatalytic activity under visible range [8,11] whereas small shifting the LSPR spectra of AuNR coated SiO$_2$ has potentially improved the stability of Au nanoparticle [7,22]. Then, we have also analyzed the LSPR shifting corresponded to the peak value, as previous plotted in Figure 3. Interestingly, the growth of LSPR shifting AuNR coated TiO$_2$ and SiO$_2$ followed the exponential growth function [23,24], such as

$$\Delta \lambda(t) = m(n_c - n_s)[1 - \exp(-2t / \delta)]$$

(2)

where $m$ is the change of wavelength per refractive index unit (RIU), $n_c$ is refractive index of material coating, in this case $n_c = 2.51$ for TiO$_2$ and $n_c = 1.47$ for SiO$_2$, $n_s$ is refractive index medium ($n_s = 1.33$), $\delta$ is the growth length, and $t$ is the thickness of the coating. Then, we have carried out a fitting process to determine the value of $m$ and $\delta$ based on this function. The value of AuNR coated TiO$_2$ are $m = 452$ nm/RIU and $\delta = 64.8$ nm and for SiO$_2$ are $m = 360$ nm/RIU and $\delta = 31.4$ nm. From this result showed the growth length of Au coated TiO$_2$ was higher than coated SiO$_2$. The peak and fitting value of LSPR shifting AuNR coated TiO$_2$ and SiO$_2$ was presented in Figure 3.

![Figure 3. LSPR peak versus the thickness from the data simulation and fitting growth function.](image)

Furthermore, we have also produced the near-electric field image of LSPR AuNR coated TiO$_2$ and SiO$_2$ both longitudinal and transverse mode for the thickness from 2nm to 20nm. The near-electric field image was shown in Figure 4(a) for Au@TiO$_2$ and Figure 4(b) for Au@SiO$_2$ both longitudinal and transverse mode. For longitudinal mode, the near-electric field of Au@TiO$_2$ and Au@SiO$_2$ appeared dawn among interface Au/TiO$_2$ and Au/SiO$_2$ at around 8nm. It means that the magnitude of the electric field increased as the thickness increased [9]. At the interface between Au and TiO$_2$ (e.g.,
longitudinal mode and also Au coated titania shows near-electric field higher than coated silica. The transition happened at thick 8nm as well.

Figure 4. The near-electric field map LSPR peak in longitudinal mode and transverse mode (a) Au@TiO$_2$ and (b) Au@SiO$_2$. For thickness $t=0$nm is Au pure and transition between $t=6$nm and $t=8$nm observed in the interface Au with TiO$_2$/SiO$_2$ both longitudinal and transverse mode.
Thus, we have also produced the near-electric field distribution of the multiple peaks from the inset Figure 2(a) for longitudinal mode and Figure 2(b) for transverse mode as shown in Figure 5. The multiple peaks display a similar near-electric field pattern for longitudinal mode thick 2nm-20nm (Figure 5(b)) so that it’s a supporting confirmation as the interband transition of Au nanoparticle [9]. In Figure 5(a)-lower row is a higher order transition from quadrupole to hexapole happened for thickness above 8nm, where the energy quadrupole higher than hexapole. This transition exists for a big particle like increasing volume [26]. The energy transition (quadrupole-hexapole) appear at the interface between gold and titania coincide with decreasing the intensity of LSPR.

4. Conclusion
In conclusion, we have performed AuNR coated TiO$_2$ and SiO$_2$, respectively by MNPBEM simulation. The result suggests that LSPR spectra of AuNR coated SiO$_2$ more stable than uncoated and the shifting of LSPR spectra can be tuned by increasing the thickness of TiO$_2$ under visible light-near infrared. The shifting AuNR coated SiO$_2$ was much smaller than AuNR coated TiO$_2$, about 807±12 nm for AuNR@SiO$_2$ and 1015±81.3 nm for AuNR@TiO$_2$ with thick 20nm. According to the fitting method, the maximum thickness of AuNR@SiO$_2$ around 42±14.1 nm and unseen for AuNR@TiO$_2$ under visible light-NIR. Based on our result, AuNR coated SiO$_2$ is the best candidate to control the stability of LSPR gold nanorod under visible light – NIR. On the other hand, for photocatalytic enhancement, the TiO$_2$ within anatase phase is good material coating aim to improved the photocatalytic activity.
under visible light-NIR. For future projects, it can be used to consider the effective thickness of Au@TiO$_2$ or Au@SiO$_2$ in conducting an experiment.

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