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Study on the effect of nanoparticle bimetallic coreshell Au-Ag for sensitivity enhancement of biosensor based on surface plasmon resonance

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Abstract. Bimetallic Au-Ag core-shell, a type of composite spherical nanoparticle consisting of a spherical Au core covered by Ag shell, have been used as active material for biomolecular analyte detection based on surface plasmon resonance (SPR) spectroscopy. SPR technology evolved into a key technology for characterization of biomolecular interaction. In this paper, we want to show the influence of nanoparticle bimettalic Au-Ag coreshell for optic respon of LSPR biosensor through attenuated total reflection (ATR) spectrum. The method consist of several steps begin from make a model LSPR system with Kretschmann configuration, dielectric function determination of composite bimetallic coreshell nanoparticle using effective medium theory approximation and the last is reflectivity calculation for size variation of core and shell bimetallic nanoparticle. Our result show that, by varying the radius of core and shell thickness, the peak of the reflectivity (ATR spectrum) shifted to the different angle of incident light and the addition of coreshell in SPR biosensor leads to enhancement the sensitivity.

1. Introduction

Recently, sensor based on localized surface plasmon resonance (LSPR) have attracted considerable attention because of its revolutionary technology [1]. The advantages brought about by curret LSPR technology include label free analysis, monitors the interaction real time, non-destructive technique, large tuneability from the visible into the infrared (IR) spectrum region, high sensitivity and selectivity. LSPR is a kind of electromagnetic resonances that exist when there is an interface between metal and dielectric material and this system have been use for sensing various biomolecules [2, 3]. When the biomolecules comes in contact to the metal film surface, that biomolecules get adsorbed on its surface and increasing the refractive index resulting in the change in the angle resonance. This LSPR properties are very sensitive to size, shape and the surrounding medium refractive index of metal nanoparticle or the medium that kept contact with metal. Tuning of the LSPR spectrum is the key issue in application such as in cancer treatment, bio medical diagnosis, enzyme detection, food safety and cellular imaging [4]. The Au-Ag bimetallic coreshell nanoparticle is one of the metal that have attracted extensive interest due to the addition of a second metal shell, changing the surface plasmon band, and enhancing the stability [5, 6]. The LSPR of Ag nanoparticle is located around 400 nm, whereas the LSPR of Au nanoparticle is located around 520 nm. The combination of that two metal is similar to combine the plasmon feature of each metal become the new plasmon feature that depend on the size and shape of core and shell that coreshell. The performance of the biosensor base on the LSPR depends on the adsorption of the biomolecule and enhancement of the field intensity of the excitation light. It has been reported that the addition other medium over metal film improves the sensitivity of the biosensor [5]. In this latter, we have been investigate the ATR spectrum of four and five mutilayer biosensor based on LSPR with Au-Ag coreshell addition and DNA as sensing analyte.

2. Biosensor System base on LSPR

2.1. *Kretschmann configuration with 5 layers*

In our study, we use the theory and computational approximation to determinate effective permittivity of composite AuAg coreshell and calculate reflectivity in attenuated total reflection (ATR) spectrum. The LSPR system using the Kretschmann configuration [7] with 5 layers, prism/Ag/coreshell/DNA/DNA+water, is shown in figure 1. θ_i and θ_r are the incident and the reflection angle , k_z is the wave vector component at *z* axis, and *d* is the thickness of the each layer.

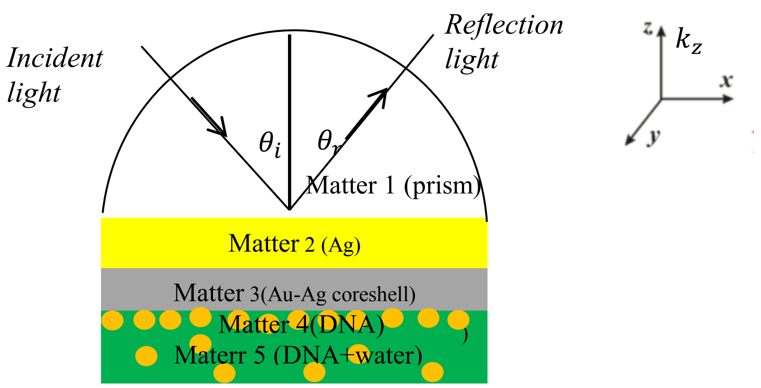

Figure1. Biosensor base on LSPR with Au-Ag coreshell

In this simulation have been carried out for wavelength 628,5 nm and the refractive indices of the SF10 glass prism used is 1,7230. The refractive indices of silver is *n*=0,13455 and extinction *k*=3,98651, the refractive indices of the gold is *n*=0,19715; *k*=3,0899 [8] , for DNA is *n*=1,335; *k*=0 and the DNA+water is *n*=1,330,; *k*=0 [9]. The thickness of Ag film is *d*=40 nm, and for DNA *d*=30 nm Finally, the reflectivity R is given by by Fresnel equation [10]

$$R = \left|r_{ijk}\right|^2 = \left|\frac{r_{ij}+r_{jk}e^{2ik_{jz}d_j}}{1+r_{ij}r_{jk}e^{2ik_{jz}d_j}}\right|^2 \tag{1}$$

with

$$r_{ij} = \frac{k_i\varepsilon_j-k_j\varepsilon_i}{k_i\varepsilon_j+k_j\varepsilon_i} \tag{2}$$

r_{ij} is the surface reflectivity between medium *i* and medium *j*. k_{ij} is the wave vector component perpendicular to the surface, k_x is the wave vector component parallel to the surface, whereas d_j and ε_i are the thickness *j*-th layer and the *i*-th medium dielectric constant

2.2. *A spherical coreshell Au-Ag*

We choose a spherical coreshell model like figure 2. The bimetallic composite model consists of a metallic Au core of radius a_2 coated by a metallic Ag of thickness $a_1 - a_2$. The dielectric constant of metallic Au, Ag and the embedding medium are ε_2, ε_1 and ε_0 respectively.

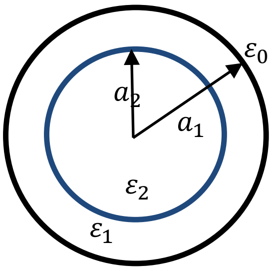

Figure 2. The Au-Ag coreshell model

In this calculation the complex form of ε_1 and ε_2 can be used from Johnson and Cristy literature [8].

2.3 Effective permittivity of coreshell
For calculating the effective permittivity of Au-Ag composite, with neglecting the correlation between the shell and core, can be employ using the Rayleigh mixture formula [11].

$$\frac{\varepsilon_{\text{eff}}-\varepsilon_0}{\varepsilon_{\text{eff}}+2\varepsilon_0} = (f_1 + f_2)(\frac{\varepsilon_{\text{incl}}-\varepsilon_0}{\varepsilon_{\text{incl}}+2\varepsilon_0}) \tag{3}$$

with

$$\varepsilon_{\text{incl}} = \frac{1-2G}{1+G}\varepsilon_1 \tag{4}$$

where

$$G = \frac{\varepsilon_1-\varepsilon_2}{2\varepsilon_1+\varepsilon_2}\left(\frac{a_2}{a_1}\right)^3 = \left(\frac{\varepsilon_1-\varepsilon_2}{\varepsilon_1+2\varepsilon_2}\right)\left(\frac{f_2}{f_1+f_2}\right) \tag{5}$$

ε_{eff} is the effective permittivity of coreshell, ε_0 is the vacuum permittivity, $\varepsilon_{\text{incl}}$ is the inclusion permittivity, ε_1 is the shell permittivity, ε_2 is the core permittivity, f_1 and f_2 are the volume fraction of the core and shell and $\frac{a_2}{a_1}$ is the rasio of core and shell radius.

2.4 Biosensor sensitivity
The calculation of the sensitivity of biosensor base on the LSPR is written [12]

$$S = \frac{\Delta\theta_{\text{sp}}}{\Delta n} = \frac{\theta_{\text{sp}}(\varepsilon_d+\Delta\varepsilon_d)-\theta_{\text{sp}}(\varepsilon_d)}{\Delta n} \tag{6}$$

Where $\Delta\theta_{sp}$ is the difference of the angle of SPR and Δn is the change in refractive index. While, the enhancement sensitivity value of LSPR biosensor with Au-Ag coreshell compare with the conventional SPR is written [13]

$$\Delta S = \frac{S_{\text{graph}}-S_{\text{kon}}}{S_{\text{kon}}} \times 100\% \tag{7}$$

3. Result and discussion
The changes of the radius of core and the thickness of shell, leads to the change of rasio $\boldsymbol{a_2/a_1}$ of the composite Au-Ag coreshell and then change the effective permittivity of composite. The increasing of effective permittivity of composite Au Ag coreshell, leads to the enhancement of the

sensitivity of this biosensor. Table 1 shows the effective permittivity of composite coreshell Au Ag that can obtained from equation (4) and depends on the rasio of radius core and shell.

Table 1. The effective permittivity of Au-Ag coreshell for the $\boldsymbol{a_2/a_1}$variation

$\boldsymbol{a_2/a_1}$	$\boldsymbol{\varepsilon}_{\mathrm{incl}}$
0.50	-14.9742 + 1.1041 i
0.90	-11.0608 + 1.1991 i
0.75	-12.9660 + 1.1612 i
1.00	-9.5086 + 1.2183 i
1.20	-5.8433 + 1.2220 i
1.30	-3.8063 + 1.1987 i

The calculated ATR spectra (reflectivity) from biosensor based on LSPR in Kretschmann configuration are shown in figure 3 and figure 4. For the layer consist only the thin film of metal, the peak of reflectivity at the angle 55 deg (*blue line*). When the coreshell composite was deposited on the surface of the metal thin film, the peak of reflectivity shifted to the large angle. From figure 3. for the a_2/a_1 of the composite is fixed at 0.9 and the thicknesses of the composite is variated from 10 nm to 40 nm, the large shift of peak is obtained for thicknesses is 40 nm but the reflectivity is small . The figure shows that at 20 nm is the best performance of the peak. From figure 4, for the thicknesses of the composite is fixed at 20 nm and the a_2/a_1 is variated from 0.5 to the 1.3, the peak shifts from the 55 deg to the 66 deg. The large shiftiness is obtained for the a_2/a_1 is 1,3 but the reflectivity is smallest from the other. Table 1 shows that for a_2/a_1=0.9 resulting the effective permittivity $\varepsilon_{\mathrm{incl}}$ =-11.0608 + 1.1991 i. Therefore at 20 nm thicknesses and ε_{incl} =-11.0608 + 1.1991 i, the shiftiness of angle is from 55 deg (*blue line*) to 57 deg (*red line*), whereas the change the permittivity is from *n*=0.13455; *k*=3.98651 (*blue line*/Ag thin film) to -11.0608 + 1.1991 i (*red line*) or *n*=0.180012 ; *k*=3.330616 . Therefore from equation (7) , calculation of the sensitivity resulting the sensitivity increase 3.636% compare with sensitivity of SPR biosensor without Au-Ag coreshell addition.

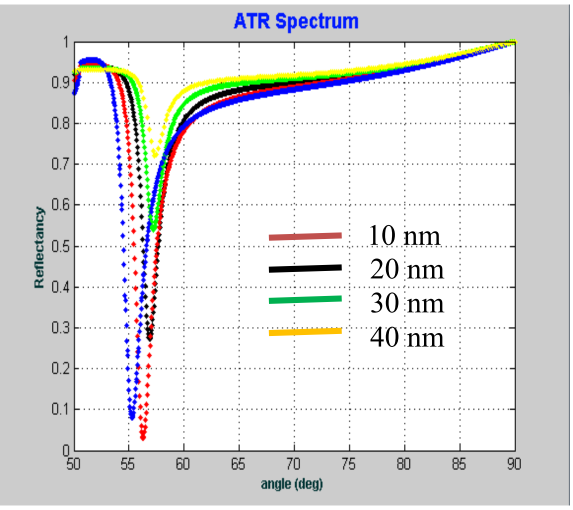

Figure 3. The reflectivity of ATR spectrum for the a_2/a_1 of the composite is fix at 0.9 and the thicknesses is variated from 10 nm to the 40 nm.

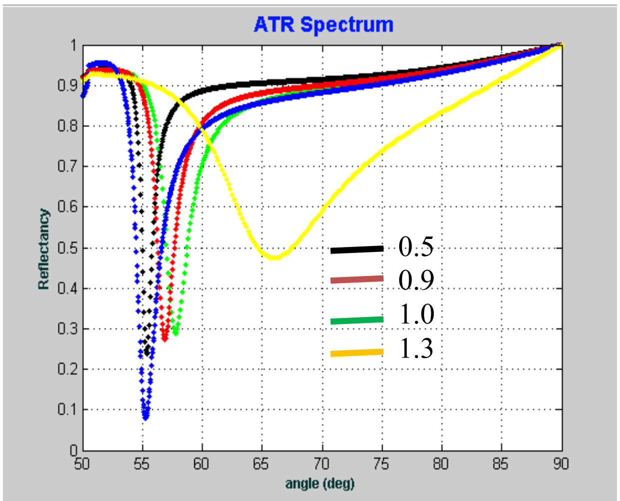

Figure 4. The reflectivity of ATR spectrum for the thicknesses of the composite is fixed at 20 nm and the a_2/a_1 is variated from 0.5 to the 1.3.

4. Conclusion

The enhancement of sensitivity of biosensor based on LSPR have been studied via the addition nanoparticle Au-Ag coreshell in LSPR 5 layer system, By variated the radius of core and shell, the refractive index of coreshell changes and leads to change the position of the peak of reflectivity spectrum to the large angle. The LSPR dips were shifted when Au-Ag coreshell were deposited on the surface of metal film (Ag). A large shift in the dip angle by that deposition suggest the potential for application in highly sensitive biosensor, in this case sensing biomolecules as analyte. The sensitivity enhancement of biosensor can be obtained from the rasio of the difference of the angle of the SPR peak with the change in refractive index.

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