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Investigating Nanoparticle-Substrate Interaction in LSPR Biosensing using the Image-Charge Theory

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Abstract — **Localized surface plasmon resonance (LSPR) has been used to develop optical biosensors. Tuning the resonance wavelength to detect target biomolecules with a particular dipolar resonance is essential when designing LSPR biosensors. In this paper, the interaction of nanoparticles (NPs) with glass substrate (SiO2) for LSPR wavelength is investigated using the concept of the image-charge theory. Using the FDTD method, it is shown how the NP and substrate size change the plasmon wavelength. Next, this phenomenon is interpreted using the analytical electrostatic eigenvalue method.**

I. INTRODUCTION

Localized surface plasmon (LSPR) resonance is associated with the collective resonances at the interface of a NP with a background media. This resonance leads to strong electric fields on the interface between the NP and its substrate at some wavelength called resonance or plasmon wavelength. Determining this wavelength is essential in LSPR applications such as surface enhanced Raman scattering (SERS) biosensors. Biomolecules are usually Raman scatterers resonating at a particular wavelength. Thus, the procedure to design a LSPR device with a desired resonance frequency is in demand for a variety of research areas. The resonance wavelength is affected by the strength of the NP-substrate interaction; thus, the material, shape, and physical dimension of both NP and media or substrate have remarkable impact on the plasmon spectrum [1].

Experiments show that increasing the background media dielectric factor red-shifts the plasmon resonance causing stronger Fano resonance [2], and accordingly more enhancements. This rule has been demonstrated for a silver-truncated tetrahedral NP, based on both the DDA (Discrete Dipole Approximation) numerical calculation method and experimental results [3]. The permittivity of the surrounding medium or refractive index per molecular binding, which is the second power of the permittivity, can be raised in at least three ways. First, larger molecules (e.g. proteins) produce larger shifts roughly in proportion to the mass of the molecules. Second, chromophores that absorb visible light couple strongly with the LSPR of NPs to produce large shifts and can be used to detect small molecules binding to protein receptors. Third, pairs of NPs that are separated by less than about 2.5 particle radii show plasmonic coupling and marked spectral shifts [4-5]. In another research, the DDA calculations implemented by Schatz et al. to model a 10 nm silver sphere either sinking into a mica substrate or surrounded by free vacuum, demonstrates that the plasmon wavelength of the sphere gets red-shifted when the sphere goes from free vacuum to being partially embedded in the mica [3]. Reducing the Au content also decreases the enhancement significantly [6]. To keep the enhancement factor in the reasonable range, we need to have a higher plasmon wavelength [7].

Although analytical methods such as Mie theory [8] are restricted to particular NP shapes, the electrostatic eigenmode method [9] has been developed to formulate the concept of image-charge for different shapes of NPs [10].

In this paper, the effect of substrate dimensions on different NP shapes including nano-ellipsoids, nano-triangles, and nano-diamonds are simulated using the FDTD method, and the results are interpreted using the analytical electrostatic eigenmode method [9, 11-14].

II. THEORETICAL BACKGROUND

Assume a quasistatic approach using a spherical NP of radius a, irradiated by z polarized light of wavelength λ, in the long wavelength limit ($a/\lambda < 0.1$). Due to this small size condition, the quasistatic estimation is a good estimation to solve electromagnetic Maxwell's equations. Therefore, Maxwell's equations can be replaced by Laplace's equation [15].

Dipole resonance modes can be investigated through the electrostatic eigenmode approximation [9, 12]. In this formulation, the surface plasmon resonances are calculated using the oscillating surface charge distribution $\sigma^k(r)$ at resonance mode k. For an arbitrary ensemble of NPs, the charge distributions can be written as a superposition of the normal modes of each NP of the ensemble as follows:

$$\sigma^k(\boldsymbol{r}) = \frac{\gamma^k}{2\pi} \oint \sigma(\boldsymbol{r_q}) \frac{(r-r_q)}{|r-r_q|^3} \hat{\boldsymbol{n}}\, dS_q \, . \tag{1}$$

Here, γ^k is k-th natural resonant mode (or eigenmode) of the nano-particle, $\varepsilon_m(\omega^k)$ is the permittivity of the metal at the $k-th$ resonance frequency ω^k, and ε_b is the permittivity of the background medium [9, 12].

The total surface charge $\sigma(\boldsymbol{r},\omega)$ at frequency ω is calculated as the weighted summation of the surface charges at every mode k:

$$\sigma(\boldsymbol{r},\omega) = \sum_k a^k(\omega)\sigma^k(\boldsymbol{r}) \, , \tag{2}$$

where $a^k(\omega)$, the excitation amplitude of the $k-th$ resonance mode is given by:

$$a^k(\omega) = \frac{2\gamma^k \varepsilon_b(\varepsilon_m(\omega^k)-\varepsilon_b)}{\varepsilon_b(\gamma^k+1)+\varepsilon_m(\omega^k)(\gamma^k-1)} \boldsymbol{p}^k . \boldsymbol{E}_0 \, . \tag{3}$$

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In the above equation, $\boldsymbol{p}^k$ is the average dipole moment of the NP at the $k-th$ resonant mode ω^k, and $\boldsymbol{E}_0$ is the incident electric field amplitude.

Resonant frequency ω^{k} is calculated using the eigenvalue at mode k and metal permittivity at this resonance frequency as follows:

$$\varepsilon_m(\omega^k) = \varepsilon_b \frac{1+\gamma^{\mathrm{k}}}{1-\gamma^{\mathrm{k}}}. \quad (4)$$

For a single spherical and in a limited range of sphere size in dipolar mode $\gamma^{\mathrm{k}} = 3$; therefore, (4) gives the resonance condition $\varepsilon_m(\omega^k) = -2\varepsilon_b$ in a limited range of NP size which will be investigated in this article

In the presence of a substrate in a background medium, the surface charges from the metal polarize both the substrate and the medium; thus, additional surface charges are created at the interface between the metal and the substrate (see Fig. 1). This phenomenon can be described by the charge-image theory [10]. As shown in Fig. 1, in this method, the combination of both substrate with electric permittivity ε_b and medium with electric permittivity ε_s is considered as an infinite individual medium with an effective electric permittivity ε_{eff}, where the metal NP has been immersed in it [13].

The electric field from the surface charges of the NP in the background medium $\sigma(\boldsymbol{r})$ at a position $\boldsymbol{r}$ induces a surface charge of $\sigma(\boldsymbol{r_1})$ at the mirror position $\boldsymbol{r_1}$:

$$\sigma(\boldsymbol{r_1}) = \frac{\varepsilon_b-\varepsilon_s}{\varepsilon_b+\varepsilon_s}\sigma(\boldsymbol{r}). \quad (5)$$

This surface charge can be imagined as the surface charge on a pseudo NP. Therefore, we can assume that we have two same interacting NPs, where electromagnetic Maxwell's equations can be analytically solved using the electrostatic eigenvalue method, if their size is much less than the incident wavelength [9, 12-14]. This interaction leads to a shift in the LSPR frequency. It has been shown that in the presence of the substrate, the excitation amplitude $\tilde{a}^k(\omega)$ at the $k-th$ mode equals to:

$$\tilde{a}^k(\omega) = \frac{2\gamma^{\mathrm{k}}\varepsilon_b(\varepsilon_m(\omega^k)-\varepsilon_b)}{\varepsilon_b(\gamma^{\mathrm{k}}+1)+\varepsilon_m(\omega^k)(\gamma^{\mathrm{k}}-1)-(\varepsilon_m(\omega^k)-\varepsilon_b)\eta T^k}\boldsymbol{p}^k.\boldsymbol{E}_0, \quad (6)$$

where

$$\eta = \frac{\varepsilon_b-\varepsilon_s}{\varepsilon_b+\varepsilon_s}, \quad (7)$$

and the interaction of the NP with the substrate is specified by the T-factor:

$$T^k = \frac{\gamma^{\mathrm{k}}}{2\pi}\oint\oint \tau^k(\boldsymbol{r})\frac{\hat{\mathbf{n}}.(\boldsymbol{r}-\boldsymbol{r_1})}{|\boldsymbol{r}-\boldsymbol{r_1}|^3}\sigma^k(\boldsymbol{r_1})dSdS_1, \quad (8)$$

which depends on the surface dipole eigenfunction $\tau^k(\boldsymbol{r})$ at the position of the NP and surface charge eigenfunction $\sigma^k(\boldsymbol{r_1})$ at the position of the mirror if the NP. The T-factor shows how strong are the interaction between the NP and its mirror; it can be approximated by the following formula for substrates with high enough thicknesses:

$$T^k = \frac{\gamma^{\mathrm{k}}}{2\pi d^3}\left(3\left(\boldsymbol{p}^k.\hat{\boldsymbol{d}}\right)^2 - \boldsymbol{p}^k.\boldsymbol{p}^k\right),$$ **(Error! Bookmark not defined.)**

where d is the distance between the centres of the NP and its mirror in the substrate.

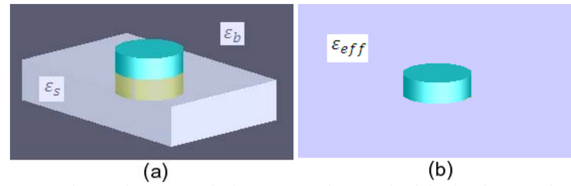

Figure 1. Charge-image technique. (a) The particel in background and its mirror in the substrate. (b) Embedding the NP in a medium with an effective permittvity.

By comparing (3) and (6), it is understood that the resonance frequency is changed in the presence of the substrate from ω^k to $\widetilde{\omega}^k$, as if the NP is entirely immersed in a medium with electric permittivity ε_{eff}:

$$\varepsilon_m(\widetilde{\omega}^k) = \varepsilon_{eff}\frac{1+\gamma^{\mathrm{k}}}{1-\gamma^{\mathrm{k}}}, \quad (9)$$

$$\varepsilon_{eff} = \varepsilon_b\frac{1+\eta T^k/(1+\gamma^{\mathrm{k}})}{1+\eta T^k/(1-\gamma^{\mathrm{k}})}. \quad (10)$$

In this paper, the effect of the substrate on the plasmon frequency on some different NP shapes is investigated. It will be shown that how the shape and size of NP and the thickness of the substrate change the effective medium permittivity ε_{eff} .

III. Simulation Results and Discussion

The finite difference time domain (FDTD) method [16] is used to investigate the effect of a glass (SiO_2) substrate on various NPs of nano-ellipsoid, nano-disks, and nano-triangles. In our simulations, the incident light is taken as a total field scattered field (TFSF) source [16] on the z-direction with polarization along the x-axis, which is along the elongation of the NPs, to get maximum efficiency.

Fig. 2 shows the ε_{eff} and the plasmon wavelength variations of a nano-ellipsoid for two minor axis sizes of 30 and 50 nm, and with the same aspect ratio along the x-axis versus the substrate thickness from 0 to 60 nm. The same simulation results is achieved when simulating a nano-disk with radii of 40 and 60 nm, and substrate thicknesses of 30 and 50 nm as shown in Fig. 3.

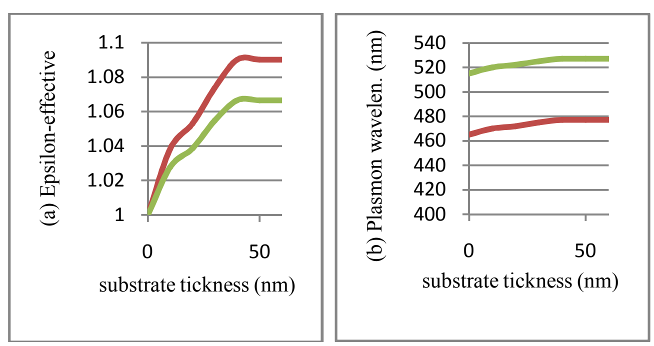

Figure 2. (a) Effective permittivity, and (b) plasmon wavelength for nano-ellipsoids with minor axis size of 30 nm (red) and 50 nm (green) and the same aspect ratio of 1.5 vs. the substrate thickness.

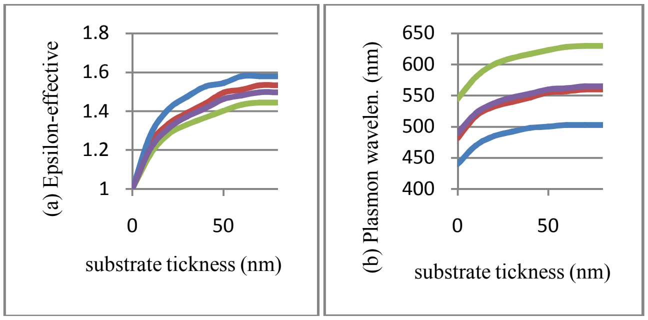

Figure 3. (a) Effective permittivity, and (b) plasmon wavelength for nano-disks with radius r, same NP thickness of 30nm, and substrate thickness t for r=40nm, t=50nm (blue); r=40nm, t=30nm (red); r=60nm, t=50nm (purple); and r=60nm, t=30nm (green).

These graphs show the same relation of the plasmon spectrum to the substrate thickness for varius radii and substrate thicknesses. The same results are extracted from simulation of nano-triangles when put on a glass substrate, as shown in Fig. 4.

These results demonstrate that increasing the substrate thickness approaches both resonance wavelength and effective epsilon to some limits. In addition, it is obvious that the larger the NP is, the less effective epsilon can be attained; thus, more plasmon wavelength is shifted towards red. The above results can be interpreted by applying the eigenmode interaction method on the charge-image theory, as explained in the previous section.

If we assume that our background is free air with $\varepsilon_b = 1$, since for every kind of substrate $\varepsilon_s \geq 1$, then $-1 \leq \eta < 0$; therefore, $\varepsilon_s \geq \varepsilon_b = 1$. Accordingly, increasing the size of NP raises the plasmon frequency and eigenvalue γ^k in the extrinsic regime [7]; according to (9), this will increase the T-factor due to more interaction between the NP and its mirror, which in turn decreases ε_{eff} in (11). Regarding T^k and γ^k being positive values and η being a negative value, we expect that $\varepsilon_{eff} \geq \varepsilon_b = 1$, where the equal sign is fulfilled for the no-substrate case ($T^k = 0$). Therefore, since the T-factor for high enough substrate thicknesses is independent to the substrate thickness, increasing the substrate thickness raises ε_{eff} from one towards a ceiling value according to (9-11).

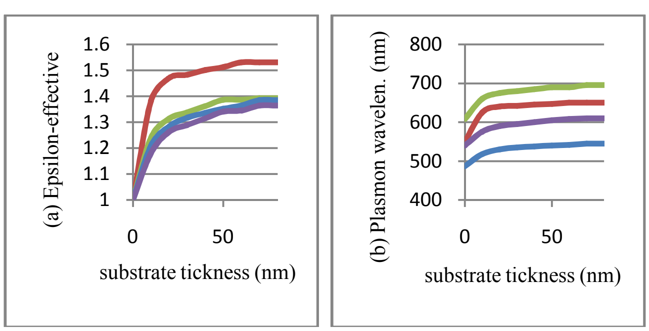

Figure 4. (a) Effective permittivity, and (b) plasmon wavelength for nano-triangles with height h, same NP thickness of 30nm, and substrate thickness t for h=75nm, t=30nm (red); h=105nm, t=30nm (green); h=75nm, t=50nm (blue); and h=105nm, t=50nm (purple).

Another conclusion that can be drawn from the simulation results is that in the absence of a substrate, for shapes with two bases like disks and triangulars, the same enhancements are observed at tips along the polarization angle on both upper and lower bases. However, using a substrate with electric permittivity higher than the medium (here free air), leads to more enhanced electric fields at the tips on interface base between the NPs and their substrates. This result has been proved by comparing Fig. 5 and Fig. 6 for nano-disks with size of 56 nm, thickness of 30 nm, and substrate thicknesses of 0 and 30nm, respectively. In addition, more enhancements are pronounced when using a glass substrate.

One more important factor which must be considered in LSPR design is the sharpness of the plasmon spectrum. According to our simulation results, using a thicker glass substrate more flattens the spectrum and creates peaks in low range wavelengths (blue range) due to multipole excitations. This defect can be compensated by increasing the NP size, as seen in Fig. 7 and Fig. 8. Fig. 7 shows the cross sections of two nano-disks with radii of 40 nm, NP thicknesses of 30 nm, and the substrate thicknesses of 20 and 80 nm, respectively. Similar graphs for two nano-disks with radii of 25 and 50 nm, NP thicknesses of 30 nm, and substrate thicknesses of 30 nm are shown in Fig. 8. The figure demonstrates how increasing the size of NPs on a substrate can compensate the effect of multipoles created in the spectrum due to the presence of a substrate.

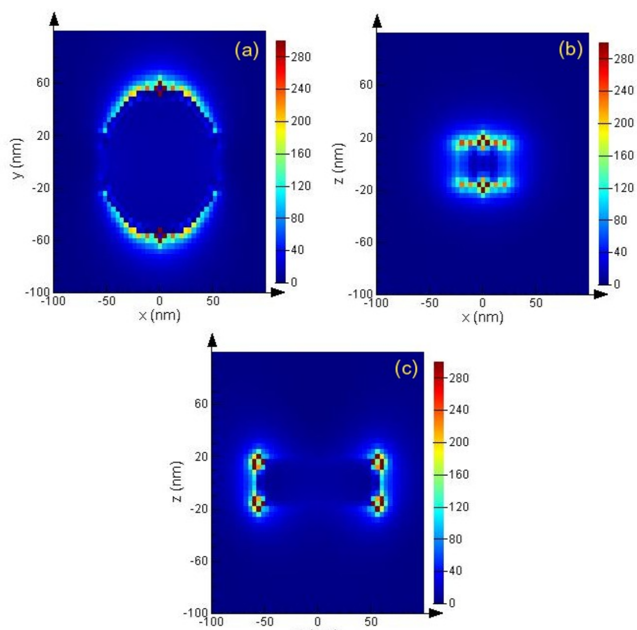

Figure 5. Total electrical field intensity on (a) plane xy on the upper base (z=15 nm), (b) plane xz passing the right tip (y=56 nm), and (c) plane yz passing the middle (x=0 nm) of a disk with radius of 56 nm and thickness of 30 nm, without using any substrates.

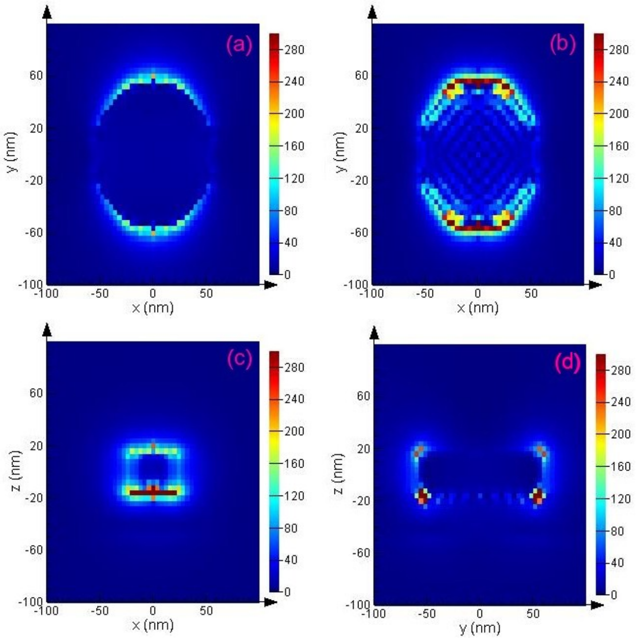

Figure 6. Total electrical field intensity on (a) plane xy on the upper base (z=15 nm), (b) plane xy on the lower base (z=-15 nm), (c) plane xz passing the right tip (y=56 nm), and (d) plane yz passing the middle (x=0 nm) of a disk with radius of 56 nm and thickness of 30 nm, using a substrates with thickness of 30 nm.

IV. CONCLUSION

We investigated the effect of substrate on the LSPR spectrum of silver NPs. Using the image-charge theory, we concluded that putting a NP on a glass substrate affects the plasmon spectrum as if another same pseudo NP has been put next to the main NP in an infinite media with the effective electric permittivity ε_{eff} for combination of the media and the substrate which is calculated using the electrostatic eigenmode method. Due to interaction between the main and NP and its image, more enhancements on the interface of the NP and the substrate are expected than between the main NP and its background media. Increasing the size of NPs results in the red-shift of the plasmon wavelength and leads to a smaller effective electric permittivity. In contrary, increasing the substrate thickness leads to rising of both effective permittivity and plasmon wavelength marginally approaching to a limit, depending on the shape and size of the NP.

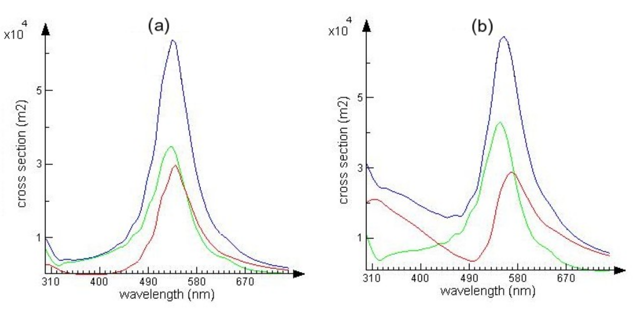

Figure 7. Cross sections of two nano-disks with radii of 40 nm, NP thicknesses of 30 nm, and glass substrate ticknesses of (a) 20 nm and (b) 80 nm, respectively.

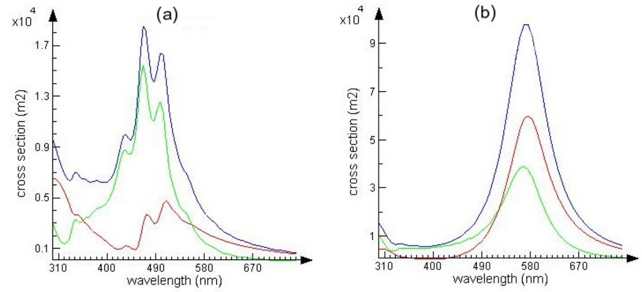

Figure 8. Cross sections of two nano-disks with NP thicknesses of 30 nm, and glass substrate ticknesses of 30 nm, and NP radii of (a) 25 nm and (b) 50 nm, respectively.

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