Effects of receptor thickness on localised surface plasmon resonance sensing performance

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Metal nanoparticles (MNPs) have potential uses in biochemical sensing applications owing to their localised surface plasmon resonance (LSPR) characteristics. In practice, selective biochemical sensors based on LSPR are constructed by MNPs and selective receptors for specific biochemical molecules. This Letter studies the effects of receptor thickness on LSPR sensing properties experimentally and theoretically. Experimental results demonstrate that an increase in polymethyl methacrylate (PMMA) receptor thickness induces a red shift of LSPR spectrum. For a 42 nm PMMA receptor, the maximum extinction efficiency is more sensitive to the test chloroform vapour than the peak wavelength. This receptor thickness effect is confirmed by electrodynamics calculations: a relatively thin receptor layer will create high peak wavelength sensitivity and low extinction efficiency sensitivity. However, it is the opposite for a relatively thick receptor layer. The turning point between thick and thin is approximately 20 nm in this Letter. These insights can be used as guidelines in fabricating high-sensitive LSPR-based biochemical sensors.

1. Introduction: Studies of localised surface plasmon resonance (LSPR)-based sensors have attracted increased interest in the past decade owing to their cost-effectiveness, high spatial resolution and small molecule sensitivity [1]. In LSPR, metal nanoparticles (MNPs) absorb and scatter light, resulting in an extinction spectrum with a specific peak. Both the wavelength and the extinction efficiency at the peak are sensitive to changes in local refractive index (RI) induced by adsorbate at the MNPs surface. Owing to these characteristics, LSPR-based sensors have potential applications in detection of both liquid phase biochemical molecules and gas phase chemicals, including streptavidin [2], anti-biotin [3], concanavalin [4], organophosphorous pesticides [5], hydrogen peroxide [6], ammonia [7], chloroform, methanol [8], toluene, ethanol and m-xylene [9–11].

Generally, selective chemical and biochemical sensors based on LSPR are constructed by MNPs, selective receptors and the corresponding biochemical analyte [12–14]. Since it senses with a non-propagating electromagnetic field, an LSPR sensor responds to the RI of its analyte only to a depth of tens of nanometres [15, 16]. This significantly emphasises the importance of dielectric layers thicknesses, including receptor layer and adsorbate layer.

Few Letters have addressed LSPR response to dielectric layers. Haes et al. [17, 18] showed in the case of single dielectric layer-coated MNPs that the shift of LSPR spectrum exhibited an essentially exponential decay until saturation. The magnitude of the LSPR shift was then determined by the formation of MNPs’ shape, size and composition, as well as the dielectric layer thickness, d. The latter determination has been experimentally quantified by Tomas Rindzevicius et al. for nanoholes and nanodisks, which were deposited with multi-layer stacks of 22-tricoseneonic acid by Langmuir–Blodgett technique [19].

However, in the case of bilayer dielectric-coated MNPs for selective LSPR sensors, the thicknesses of dielectric layers, especially the receptor layer, not only have significant impact on their LSPR properties, but also on their sensing performance. In this Letter, the authors study such effects by utilising a typical two-dimensional array of silver triangular nanoprisms with its receptor layer of polymethyl methacrylate (PMMA) and analyte layer of chloroform. Both the nanoparticles and the receptor layer in this Letter are of significant interest in chemical sensing applications [20–22]. Following the chloroform adsorption experiment, a numerical model for LSPR sensing process is created and the finite-difference time domain (FDTD) method is employed to confirm the experimental results and to further explore the effect of receptor thickness on LSPR sensing performance.

2. Experimental results: The regular ordered silver triangular nanoprisms array on glass substrates was fabricated by nanosphere lithography (NSL), the most popular means to produce nanoscale structures owing to its cost-effectiveness and its speed in producing large area periodic arrays with a specific particle shape, placement and orientation. The fabrication process primarily consists of three steps: first, a layer of ~430 nm polystyrene (PS) nanospheres colloidal suspension was spin-coated onto the substrate to form a large-area close-packed nanospheres monolayer pattern by selecting the proper solution concentration, spin-coating conditions and surface properties; second, a layer of ~50 nm silver was deposited on the monolayer template in a thermal evaporator (400-I, C-Vac Inc., China); and third, the PS nanospheres were removed by sonication in ethanol, and the well-ordered two-dimensional triangular nanoprisms array was finally obtained on the substrate, as shown in Fig. 1.

PMMA was applied to the receptor owing to its excellent characteristics, such as long-term stability, low cost, low optical loss and no particular light absorption in the visible spectrum. Spin-coating method was employed to prepare PMMA overlayers. Using a model for LSPR-based sensors.
microsyringe, a small amount (approximately 50 μL) of PMMA solution (AR-P639.04, ALLRESISIT Inc., Germany) molecules (molecular weight is 50 kg mol⁻¹, RI is 1.49) in ethyl lactate was dispensed onto the fabricated triangular nanoprisms from a distance of 5 mm above the chip surface. Samples of PMMA overlayers were prepared for 30 s using different spin speeds, 3000, 4000, 5000 and 6000 rpm, respectively. Thin, homogeneous, transparent PMMA overlayers were obtained, and the thicknesses were measured to be 103, 78, 65 and 42 nm, respectively, by a profiler (NewView 7300, Zygo Inc., America).

The LSPR-based extinction spectra of the samples were measured in clean air at room temperature (20°C) by an UV–vis–NIR spectrometer (QE65000, Ocean Optics Inc., America), with associated data processing software. Spectra results indicate that an increase in the thickness of PMMA overlayer induces a red-shift of the peak wavelength and a decrease of maximum extinction efficiency. In the case of bare silver triangular nanoprisms without PMMA overlayer, the LSPR spectrum presents a resonance peak \( \lambda^0 \) of 626 nm and a maximum extinction efficiency \( E^0 \) of 0.28, as indicated in Fig. 2a. For samples with a 42 nm PMMA overlayer, \( \lambda^0 \) locates at 669 nm, differing by 43 nm from that without PMMA overlayer. The maximum extinction efficiency for the latter case is 0.275, decreasing by 1.8%. This decrease in extinction efficiency can be attributed to the small quantity of light absorption of PMMA. Measured spectra results for three other cases of PMMA thicknesses are also presented in Fig. 2a.

The peak wavelength \( \lambda^0 \) as a function of PMMA thickness \( d \) is shown in Fig. 2b. As \( d \) increases from 0 to 103 nm, the increase of \( \lambda^0 \) is initially rapid and then slows down, suggesting an exponential relationship. This trend of change in \( \lambda^0 \) with the change in \( d \), highly consistent with previous studies [17, 18], is based on the plasmon resonance theory that the amplitudes of the electric field (E-field) decay exponentially as the distance increases from the dielectric/metal interface [16].

To evaluate the sensing performance of the samples, we performed analyte adsorption experiments. Chloroform, a sensitive material to PMMA [21, 23], was the analyte in our experiments. When exposed to different concentrations of chloroform, the LSPR sensor chip exhibits different spectra responses. Fig. 3 shows such responses for a sample with a 42 nm PMMA overlayer. As indicated in Fig. 3a, as the chloroform concentration increases from 0 to 680 ppm, the maximum extinction efficiency \( E^* \) of the LSPR spectrum decreases gradually, suggesting an approximately linear relationship (Fig. 3b). However, the peak wavelength \( \lambda^* \) nearly holds still at approximately 665 nm in this process. This spectrum response is essentially a response to changes in RI induced by chloroform concentration at the sample surface: the higher the concentration, the greater the RI changes, and as a result, the more the spectrum movements.

To evaluate the sensing performance of the sensor chip, we define ‘extinction efficiency sensitivity (EES)’ by \( \alpha_{E_{ext}}(\lambda) = \frac{P_{E_{ext}}(\lambda)}{P_{E_{inc}}(\lambda)} \) and ‘peak wavelength sensitivity (PWS)’ by \( \alpha_{D_{peak}}(\lambda) = \frac{P_{D_{peak}}(\lambda)}{P_{D_{inc}}(\lambda)} \), where \( \Delta E \) and \( \Delta D \) are the variations in extinction efficiency and peak wavelength at different vapour concentration, with \( \Delta C \) being the corresponding concentration change. As indicated in Fig. 3, the 42 nm PMMA functionalised LSPR sensor chip has a relatively great EES, approximately \( 4.76 \times 10^{-7} \) ppm⁻¹, and an inconsiderable PWS, almost 0 nm/ppm. This sensing property indicates that the maximum extinction efficiency is more sensitive than the peak wavelength to the RI changes for the 42 nm PMMA functionalised LSPR sensor chip.

3. Numerical simulations: To confirm the spectra behaviour of LSPR sensor described in Section 2 and to further understand the effects of receptor thickness on LSPR sensing properties, we performed numerical simulation by employing the FDTD method (FDTD Solution, Lumerical Inc., Canada). The FDTD method [24] is well suited for studying the LSPR properties of MNPs, as it is known to generate accurate results when used for this application [25–27]. The FDTD numerical method evaluates the interaction of light with electrons of metal in the time domain. The intensity of the electromagnetic field for an arbitrary spot in the space can be obtained by solving the transverse magnetic (TM) and the transverse electric (TE) Maxwell’s curl equations in the Yee form [28, 29]. Given the surface area of the nanoparticle, \( S \), the extinction efficiency was obtained by

\[
\alpha_{E_{ext}}(\lambda) = \frac{P_{E_{ext}}(\lambda)}{P_{E_{inc}}(\lambda)} \tag{1}
\]

where the power transmission parameter \( P \) was obtained by the Poynting vector: \( P = E \times H \), with the subscripts ext and inc representing the extinction power of emergent light and the power of incident light, respectively. To ensure consistency with the experiment, the metal material was set to be silver, with its complex relative dielectric constant \( \varepsilon_m \), obtained from Palik [30]. The substrate was assumed to be glass with thickness \( d_s \) of 1 mm and RI of 1.51 in our simulation, and the receptor layer was a non-light tight material with a bulk RI of 1.49 to be PMMA. The illumination was performed under normal incidence and modelled as non-polarised in order to imitate natural light. In the calculations, the mesh accuracy was set to 5 with perfectly matched layer boundary condition.

The numerical model of LSPR-based sensors is depicted in Fig. 4. Silver triangular nanoprisms are arranged in a hexagonal form, with a height \( h \) of 50 nm and a period of 430 nm, as shown in Fig. 4a. It should be noted in Fig. 4c that when the height of receptor \( t < h \), all the PMMA was filled in air gaps among the silver triangular nanoprisms. However when \( t > h \), part of the PMMA was a filler among nanoprisms and another part was a film formed on top of them with a thickness of \( d = t - h \), where \( h = 50 \) nm in the simulation.

Here in our numerical simulation, the height of receptor for each test case ranges from \( t = 0 \) to 200 nm, with increment of 10 nm. The calculation results of six typical heights shown in Fig. 5a indicate that an increase in the receptor height \( t \) induces a red shift of LSPR spectrum and an increase of extinction efficiency. For \( t = 0 \) nm, the peak of the extinction spectrum is located at
615 nm, which is slightly smaller than the experimental result shown in Fig. 2. This is because the characteristic sizes and shapes of fabricated nanostructures array are not as homogeneous as considered in the simulation. Also, for $t = 150$ nm, that is, the thickness of PMMA layer $d = 100$ nm, the peak wavelength $\lambda^*$ of the extinction spectrum is 699 nm approximately, which is close but not absolutely equal to 702 nm, the experimental result for 103 nm PMMA layer shown in Fig. 2.

The peak wavelength $\lambda^*$ of the extinction spectrum as a function of the receptor height is plotted in Fig. 5b. As receptor height increases from 0 to 200 nm, increase in $\lambda^*$ is initially rapid and then slows down, suggesting an exponential relationship, which closely matches the experimental results shown in Fig. 2b. When $t = 160$ nm, the extinction spectrum has a $\lambda^*$ of 703 nm, differing by 88 nm from that of $t = 0$ nm. However, when $t$ increases from 160 to 200 nm, the peak wavelength $\lambda^*$ almost holds still at 703 nm. This phenomenon indicates that when the thickness of PMMA layer $d < 110$ nm, the triangular nanoparticles locate in a local RI environment, and the extinction spectrum responds to an equivalent RI. But a thicker PMMA layer than 110 nm will create a bulk RI of 1.49, and thus the extinction spectrum holds still. At this point, the decay length of LSPR in this case is approximately 110 nm.

Calculations of RI sensitivity are then performed to further investigate the effect of receptor thickness on LSPR sensing performance. Results indicate that both the peak wavelength $\lambda^*$ and the maximum extinction efficiency $E^*$ of the extinction spectrum change with the environmental RI. Figs. 6a and b present two typical instances. When the receptor height $t = 50$ nm, the peak wavelength $\lambda^*$ varies approximately linearly with RI, as indicated in the inset of Fig. 6a, with its slope, $m_1 = \Delta \lambda^*/\Delta n$, denoting the peak wavelength RI sensitivity (PWRIS), where $\Delta \lambda^*$ and $\Delta n$ are peak wavelength shift and the corresponding refractive index change [31]. When the receptor height $t = 100$ nm, the maximum extinction efficiency $E^*$ decreases as RI increases, suggesting a linear relationship, as indicated in the inset of Fig. 6b. Similarly, we introduce ‘extinction efficiency RI sensitivity’ (EERIS), which is defined by $m_2 = \Delta E^*/\Delta n$, where $\Delta E^*$ and $\Delta n$ denote maximum extinction efficiency change and the corresponding refractive index change, respectively.

It should be noted that the parameter EERIS resembles EES in Section 2. Both of them describe the maximum extinction efficiency changes with the medium in different ways, and they will be identical when the vapour concentration ppm is scaled in RI. So are the parameters PWRIS and PWS. Comparing Figs. 6a with b, the PWRIS for $t = 50$ nm is approximately 160 nm/RIU, much higher than that for $t = 100$ nm, approximately 0 nm/RIU. On the contrary, the EERIS for $t = 50$ nm is approximately 0.5415 RIU$^{-1}$, much lower than that for $t = 100$ nm, approximately 1.255 RIU$^{-1}$.

The PWRIS and EERIS as a function of receptor height $t$ are presented in Figs. 6c and d. As in the case of PWRIS, $m_1$ falls rapidly from 427 to 0 nm/RIU as $t$ increases from 0 to 90 nm, and will keep still at 0 nm/RIU for $t > 90$ nm. This indicates that the presence of receptor has greatly weakened the peak wavelength sensitivity of MNPs. It is well known that the resonant wavelength senses with the electromagnetic fields that only exist in the range of the decay length and decay exponentially on top of the surface of MNPs. Thus, a large distance of the analyte from the MNPs, that is, a high receptor, will induce a poor peak wavelength response.

However, in the case for EERIS as indicated in Fig. 6d, $m_2$ increases from 0 to 1.4 RIU$^{-1}$ as $t$ increases from 30 to 200 nm, first rapidly and then slows down. This is because the changes in RI will induce the overall variation in extinction efficiency of LSPR spectrum, and RI changes with a high receptor will induce a greater change in extinction efficiency.

Specifically, when $t \leq 70$ nm, that is, the receptor layer thickness $d \leq 20$ nm, the sample has a relatively poor EERIS that $m_2 < 1$ RIU$^{-1}$, and a relatively good PWRIS that $m_1 \geq 60$ nm/RIU. However, when $d > 20$ nm, with the PWRIS grows inconspicuously, EERIS become prominent with $m_2 > 1$. For instance, when $t = 90$ nm, that is, the PMMA layer thickness $d = 40$ nm, the PWRIS is 0 nm/RIU, whereas the EERIS is approximately 1.15 RIU$^{-1}$. This result is highly consistent with the result of chloroform sensing experiment shown in Fig. 3. In short, the peak wavelength $\lambda^*$ is more sensitive with external dielectric environment changes than the maximum extinction efficiency $E^*$ for a relative thin receptor layer (<20 nm in this Letter), and oppositely for a relative thick receptor layer (>20 nm in this Letter), with the turning point determined by the formation of MNPs and the characteristics of receptor layer.

4. Conclusions: This Letter presents a study on the effects of receptor thickness on the optical properties and the sensing performance

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of LSPR-based sensors. Experimental results indicate that an increase in thickness of PMMA receptor film induces a red shift of LSPR spectrum, suggesting an exponential-like relationship. For 42 nm PMMA functionalised silver triangular nanoprisms, the maximum extinction efficiency sensitivity to chloroform concentrations is $4.76 \times 10^7 \text{ppm}^{-1}$, and the peak wavelength sensitivity is approximately 0 nm/RIU.

An identical trend of spectrum response to PMMA receptor thickness is found from numerical simulation results: the thicker the PMMA over-layer, the longer the resonant wavelength. When exposed in different external dielectric environments, both the peak wavelength and the maximum extinction efficiency vary. As the height of PMMA film increases from 0 to 200 nm, the PWRIS falls rapidly from 427 to 0 nm/RIU and then keeps still, whereas the EERIS increases from 0 to 1.4 RIU$^{-1}$. In general, a relatively thin receptor layer will create high peak wavelength sensitivity and low extinction efficiency sensitivity. These insights into the effects of receptor overlayer thickness on the sensing properties of LSPR-based sensors can be used as guidelines in fabrication of sensitive LSPR sensors.

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6 References


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