This is an electronic reprint of the original article.
This reprint may differ from the original in pagination and typographic detail.

Aksimsek, Sinan; Jussila, Henri; Sun, Zhipei

Graphene–MoS₂–metal hybrid structures for plasmonic biosensors

Published in:
Optics Communications

DOI:
[10.1016/j.optcom.2018.07.075](https://doi.org/10.1016/j.optcom.2018.07.075)

Published: 01/12/2018

Document Version
Peer reviewed version

Published under the following license:
CC BY-NC-ND

Please cite the original version:
Aksimsek, S., Jussila, H., & Sun, Z. (2018). Graphene–MoS₂–metal hybrid structures for plasmonic biosensors. *Optics Communications*, 428, 233-239. <https://doi.org/10.1016/j.optcom.2018.07.075>

Graphene-MoS₂-Metal Hybrid Structures for Plasmonic Biosensors

Sinan Aksimsek^{a,*}, Henri Jussila^a, Zhipei Sun^a

^a*Department of Micro- and Nanosciences, Aalto University, Tietotie 3, FI-00076 Espoo, Finland*

Abstract

Surface Plasmon Resonance (SPR) biosensors are widely used for real-time label-free detection in medical diagnostics, pharmaceutical researches and food safety. Although there is a growing interest in miniaturization of biosensors for self-detection and diagnostics at out of laboratory, the performance of conventional metal SPR sensors is still limited. In this paper, we theoretically propose graphene-MoS₂-metal hybrid structures based plasmon sensors under the best minimum light intensity approach, which represents the performance analysis in case of the lowest reflected light strength. It is demonstrated that the metal thickness can be reduced from 55 nm to 32 nm and 37 nm meanwhile the performance of the background sensor can be improved by 87% and 13% with the 4 additional MoS₂ and graphene layers, respectively. Besides MoS₂ based SPR devices provide much better sensitivity performance than that of graphene, our results reveal the another promising property of MoS₂, the sensitivity of SPR sensors can be greatly increased with a few number of MoS₂ within the angular SPR system while reducing the size of the device, especially for particular applications such as detecting a single molecule and biosensing at low biomolecule concentration. Furthermore, for the first time we show that the equivalent optical properties of a multilayered structure is also depend on the layer thickness which provide a novel knowledge for the next studies on 2D material based SPR plasmonic devices with the multilayered structures.

Keywords: Nanomaterials, Surface plasmons, Multilayers, Plasmonics, Biological sensing and sensors, Mathematical methods in optics.

1. Introduction

Surface plasmons (SPs), i.e. polaritons, are the light waves that propagate along the surface of a metal contacting with a dielectric, and these evanescent waves are formed by the plasma oscillations of free electrons near the metallic surface. When the resonant interaction between the incident photon ($\hbar\omega_{\text{photon}}$) and oscillations of free electrons ($\hbar\omega_{\text{plasma}}$) in the conduction band of the metal is achieved, the incident light excites surface plasmons [1]. While this phenomenon (generally known as Surface Plasmon Resonance (SPR)) has been investigated in the framework of plasmonics devices such as modulators, switches, couplers and waveguide components [2], it is also an excellent optical technique to measure the properties of the nanoscale thin films [3, 4]. In addition, SPR technique has been commonly subject to the biomolecule and chemical sensing applications [5, 6]. SPR biosensors use light to sense the optical changes in the surrounding medium. As the sensing medium (e.g. water) is doped with biomolecules, the refractive index of the medium near the metallic surface locally changes, and this change produces variations in the pattern (e.g., resonance angle, wavelength, phase, etc.) of the excitation light accordingly. Their extremely sensitive character makes SPR

25 biosensors commonly used biooptical devices in particular for real-time measurement and quantification of molecular binding kinetics such as antibody-antigen interactions, DNA hybridization, and protein bindings [7, 8]. However, the sensitivity of the best state-of-art conventional metal based SPR biosensors can be improved up to a certain limit [9, 10].

The recent years have witnessed the remarkable research effort on graphene and the other two-dimensional (2D) layered materials. Above all, graphene, a novel zero-bandgap material, has been extensively studied in the last decade due to its unique optical and electrical properties such as ultrahigh carrier mobility [11], optical opacity [12], high thermal conductivity [13] and ultrafast wideband optical response [14]. Despite being only a single atom thick ($\sim 0.34\text{ nm}$), graphene has an excellent compatibility with nanofabrication, and therefore the potential applications of graphene are enormous, ranging from solar cells to optical modulators [14, 15]. Recent researches have shown that graphene also can be used as a biomolecular recognition element (BRE) in SPR biosensors due to its strong detection capability through π -stacking force between graphene and the carbon-based biomolecules [16, 17, 18, 19, 20, 21]. However, Wu et al. reported that the angular sensitivity of conventional metal (gold substrate) SPR sensors can be improved by 25% with deposited 10 graphene layers, which is challenge at the moment for nanofabrication considering the number of layer [22]. On the other hand, it is

*Corresponding author

Email addresses: sinan.aksimsek@aalto.fi (Sinan Aksimsek),
Phone: +358-46-8422626 (Sinan Aksimsek)

also reported that the angular sensitivity of a very similar structure (silver substrate) can be reduced by increasing the number of graphene layer [23]. The contradiction on the sensing behaviors of these sensors stems from the additional 2 nm chromium adhesion layer deposited between the prism and the silver substrate in the latter design, which indicates the other layers can reverse the effect of the graphene on the sensitivity. Therefore, the alternative SPR substrate models are required for sensitivity enhancement.

“Beyond graphene”, i.e. single-layered transition metal dichalcogenides (TMDs), have shown great potential for biological applications due to their rich characteristics such as large surface area, controllable electronic and optical properties, and stability in aqueous environments [24]. Ultra-thin monolayer MoS₂ (molybdenum disulfide), a member of TMDs, is a two-dimensional semiconductor with a direct bandgap of 1.8 eV. Due to relatively weak forces between monolayers in bulk MoS₂, the formation of atomically thin films with pristine interfaces is possible from natural MoS₂ crystals [25], and by chemical-vapor deposition (CVD) method [26], and a monolayer MoS₂ is only around ~ 0.65 nm thick. MoS₂ is a biocompatible nanocrystal [27], and currently it has received attention for biosensing applications such as nanoprobe sensing platforms [28], field effect transistor based biosensors [29, 30], chemical sensors [31] and gas detectors [32]. Furthermore, MoS₂ can be stacked together with graphene to form a van der Waals-bonded heterostructure, offers great potential to design new biosensing devices with various functionalities [33, 34, 35]. Zeng et al. proposed graphene-MoS₂ SPR biosensor with Au substrate based on the phase change of the excited light [36]. However the phase sensitivity of the proposed model has an exponential characteristic which implies that the sensor gives same phase response for different analytes having relatively close refractive indices after a threshold point. Moreover, the differential phase detection scheme requires highly complicated measurement setup, and sensors based on phase detection cannot mechanically moved [37]. A different type of graphene-MoS₂ configuration was also reported with a fiber optic biosensor based on the wavelength change [38], showing a decreasing sensitivity after one layer MoS₂. Maurya et al. recently presented the sensitivity analysis of graphene and MoS₂ biosensors using silicon, demonstrates a decreasing sensitivity with both graphene and MoS₂ layers though [39].

Opposite to these results, we present here the sensitivity of graphene-MoS₂-metal hybrids can be enhanced greatly with a few number of MoS₂ layers with the angular SPR detection which is a simple measurement setup. We also performed another analysis for the proposed hybrids with graphene enhancement with TMM method. Graphene and MoS₂ were then compared in terms of the sensitivity enhancement, and it shows the sensing performance of the biosensor improves with both atomic layer. Considering the most difficult scenarios for sensing such as detecting a single biomolecule, and low biomolecule concentration,

the biomolecule layer was monolayer single stranded DNA (ssDNA) with a thickness of 3.2 nm. In our model, opposite to the previous studies, we demonstrated that the sensitivity doesn’t depend on metal thickness, and it can significantly decrease while increasing the sensitivity with atomic layer enhancement, considering the best minimum light intensity. In the background structure graphene is used as a biorecognition element due to its strong interaction capability with carbon-based molecules, and MoS₂ is deposited between graphene and the metal considering its high optical absorption efficiency (~ 10) [40]. Furthermore, considering A (~ 1.9 eV) and B (~ 2.1 eV) excitonic peak points in the absorption spectra of monolayer MoS₂ [41], and the wavelength of the most widely used HeNe laser, the incident p-polarized light is excited at 632.8 nm. We theoretically demonstrated graphene-MoS₂-metal hybrid structure can work as simple angular SPR sensors with highly improved sensitivity when the few atomic layers of MoS₂ is incorporated to sensor structure. Our results show that the sensitivity of the background structure can be improved by 87% and 13% with the 4 additional MoS₂ and graphene layers, respectively. The sensitivity can be ~ 2.3 times as large, when the metal substrate is coated with 5 layer MoS₂ and 1 layer graphene.

2. Proposed Model and Theory

2.1. Optical Properties of the Layers

The proposed atomic layered optical system is based on the well-known Kretschmann’s attenuated total reflection (ATR) configuration.

As shown in in 1(a), Ag-film is placed at the bottom of the prism, and MoS₂ is deposited between Ag-film and graphene. Graphene is in contact with the analyte to capture the carbon-based biomolecules via π -stacking interaction. The optical constants of graphene and MoS₂ are given in Table 1. We choose to use an empirical value for graphene even though the experimentally measured optical constant of graphene may slightly differ from this value [3]. Note that the permittivity is defined by $\epsilon = \epsilon' + i\epsilon''$ where the real part ϵ' represents to the stored energy and the imaginary part ϵ'' represents the energy loss within the medium.

2D material	Thickness	ϵ'	ϵ''	Referecence
Graphene	0.34 nm	7.68	6.895	[42]
MoS ₂	0.65 nm	34.17	9.44	[43]

Table 1: Optical constants of Graphene and MoS₂ at 632.8 nm.

The refractive index (RI) of SF11 is calculated as $n_1 = 1.7786$ by using its dispersion formula. The RI of the metal (Ag) is $n_2 = 0.05625 + i4.2760$ [44]. The thickness of the Ag-film is optimized during the design, therefore the reader is referred to Table 2 and Table 3 for its thickness. The optical identity of monolayer ssDNA is given by $n_5 =$

Figure 1: (a) The schematic diagram of graphene-MoS₂-metal hybrid structure based biosensor. P-polarized light is focused onto the metal through the prism and the reflected light is detected via the photodetector. (b) Excitation of surface plasmons with Kretschmann's configuration: At a certain incident angle, the tangential component of the incident wave vector equals to the wave vector of the surface plasmons which propagate along the x-direction at metal (ϵ_m)—surrounding medium (ϵ_a) interface.

1.462 and $d_5 = 3.2\text{nm}$, respectively [45]. The last layer is water, and its refractive index is $n_6 = 1.3317$.

2.2. Resonance Condition

When an incident light couple with a metallic surface which is in contact with a dielectric, free electrons induce discontinuity in the magnitude of the electric field in the direction of the surface normal. Surface plasmons have p-polarized (TM mode) character, and therefore s-polarized (TE mode) waves don't support the plasmons due to not having any $\vec{E}$ component in the direction of the surface normal.

Electric and magnetic field components of p-polarized incident light are given by

$$\vec{E}_i = (E_{ix}, 0, E_{iz})e^{i(k_{ix}x + k_{iz}z - \omega t)} \quad [\text{V/m}] \quad (1)$$

and

$$\vec{H}_i = (0, H_{iy}, 0)e^{i(k_{ix}x + k_{iz}z - \omega t)} \quad [\text{A/m}] \quad (2)$$

respectively. By introducing (1) and (2) into source free Maxwell's Equations, and then applying the related

boundary conditions [46], the resonance condition is derived as follows:

$$\frac{2\pi}{\lambda} \sqrt{\epsilon_p} \sin \theta_{RES} = \frac{\omega}{c} \sqrt{\frac{\epsilon_m \epsilon_a}{\epsilon_m + \epsilon_a}} \quad (3)$$

where λ is the wavelength of the incident light, ω is the angular frequency of plasmon, c is the speed of light, θ_{RES} is the resonance angle, ϵ_p , ϵ_m and ϵ_a are the permittivities of the prism, SPR metal and the adjacent medium, respectively.

Note that the right hand side of the dispersion equation (3) defines the wave vector of the surface plasmons propagating along the x-direction at metal-dielectric interface:

$$k_{sp} = k'_{sp} + ik''_{sp} \quad [m^{-1}] \quad (4)$$

where k'_{sp} and k''_{sp} represent the propagation index and absorption index of SPs wave vector, respectively. Surface plasmons decay along the x-direction by a factor of $\exp(-2k''_{sp}x)$, and the propagation length is determined as follows:

$$L_{sp} = \frac{1}{2k''_{sp}} \quad [m] \quad (5)$$

2.3. Transfer Matrix Method (TMM)

2x2 Transfer Matrix Method (TMM) is a simple and efficient technique, and is employed with Fresnel Equations to derive the reflected light intensity of the proposed multilayer optical structure. It is assumed in the formulation that all semi-infinite layers, parallelly placed along the z-direction, are isotropic. The schematic of the generalized multilayered optical system is illustrated in Fig 2.

Figure 2: The schematic illustration of N -layered optical system. $\vec{E}$, $\vec{H}$, ϵ , n and d represent electrical field, magnetic field, permittivity, refractive index and thickness related to any layer, respectively. In the most general sense, the field terms in each layer are written as the summation of forward and backward waves, i.e. $\vec{E}_N = \vec{E}_N^+ + \vec{E}_N^-$.

The boundary conditions imply that the field components parallel to the surface must be continuous in this N -layer model, which is leading:

$$\begin{bmatrix} \vec{E}_1 \\ \vec{H}_1 \end{bmatrix} = M \begin{bmatrix} \vec{E}_{N-1} \\ \vec{H}_{N-1} \end{bmatrix} \quad (6)$$

where $\vec{E}_1$, $\vec{E}_{N-1}$, $\vec{H}_1$ and $\vec{H}_{N-1}$ represent the tangential components of electric and magnetic fields at the first and the last boundary, respectively. M presents the system Transfer Matrix of the optical layered system and is given as [47, 36]:

$$M = \left(\prod_{k=2}^{N-2} M_k \right)_{ij} = \begin{bmatrix} M_{11} & M_{12} \\ M_{21} & M_{22} \end{bmatrix} \quad (7)$$

where

$$M_k = \begin{bmatrix} \cos \gamma_k & -i \sin \gamma_k / \eta_k \\ -i \eta_k \sin \gamma_k & \cos \gamma_k \end{bmatrix} \quad (8)$$

From equation (7), the reflected and transmitted light intensity of N-layer optical system in case of p-polarization are derived as follows:

$$R_I = \left| \frac{(M_{11} + M_{12}\eta_N)\eta_1 - (M_{21} + M_{22}\eta_N)}{(M_{11} + M_{12}\eta_N)\eta_1 + (M_{21} + M_{22}\eta_N)} \right|^2 \quad (9)$$

and

$$T_I = \frac{n_1 \cos \theta_N}{n_N \cos \theta_i} \left| \frac{2\eta_1}{(M_{11} + M_{12}\eta_N)\eta_1 + (M_{21} + M_{22}\eta_N)} \right|^2 \quad (10)^{205}$$

where

$$\eta_k = \frac{\cos \theta_k}{n_k} = \frac{(\varepsilon_k - n_1^2 \sin^2 \theta_i)^{1/2}}{\varepsilon_k} \quad (11)$$

and

$$\gamma_k = \frac{2\pi d_k}{\lambda} (\varepsilon_k - n_1^2 \sin^2 \theta_i)^{1/2} \quad (12)^{210}$$

Here, η_k , ε_k and d_k demonstrate the impedance, the permittivity and the thickness of k th layer, respectively.

3. Results and Discussion

3.1. Optimization of Biosensor Structure

According to the conventional optimization approach, the thickness of the noble metal is determined at first, and thereafter the sensing performance of the enriched substrate is examined [22, 23]. However, here, the metal was first coated with atomic layers, and then its thickness was optimized according to minimum intensity. It is obvious that the lower the minimum intensity, the larger is the surface plasmons' amplitude. The proposed atomic layered biosensor structure was simulated by applying TMM technique with the optical properties of the 6-layer system. Background substrate consists of Ag, monolayer MoS₂ and monolayer graphene, and in each step a new layer, graphene or MoS₂, was added. As shown in Fig. 3, the resonance angle of pure Ag substrate without any atomic layer is at 52.11°, while this resonance occurs at the angle of 52.75° for Ag with 1 layer (L) MoS₂. Therefore, the change in resonance angle is 1°/nm due to added MoS₂ monolayer. Furthermore, the resonance angle of the background (Ag film-1L MoS₂, 1L graphene) is at 52.91°,

Figure 3: SPR spectra of the pure metal (Ag), Ag+ 1L MoS₂ and background structures.

which is referred to 0.47°/nm SPR angle shift due to added 1L graphene according to Fig. 3. Table 2 shows that ensuring the minimum light intensity gives a better contrast in SPR spectra, and the resonance angle position shifts slightly less than 0.6°/nm for added graphene layers (~0.2° change in θ_{RES} w/o ssDNA medium), and this value is exactly matched with the same parameter observed experimentally for the gold (Au)-graphene sensor in Ref [3]. In both tables, the reflected light intensity tends to decrease with the number of graphene and MoS₂ layers, implying the amount of the absorbed light by atomic layers increases. The SPR spectra in accordance with the number of graphene and MoS₂ layers with respect to the incidence angle is plotted in Fig. 4(b) which is a clear illustration of another attitude, coating with MoS₂ makes SPR curves more wider (rise in FWHM) than graphene coating due to both its higher absorption and thickness than that of graphene.

Next, we summarize the results from the SPR curves with and without the monolayer ssDNA molecules in Table 2 and Table 3. As explained, the resonance angle will shift after the presence of the biomolecule due to the change in the refractive index. Table 2 indicates that the shift in the resonance angle $\Delta\theta_{RES}$ increases with the number of graphene layer. Although the change in $\Delta\theta_{RES}$ is not bigger than 0.01° per layer, this parameter improved by 13% after the 4 additional graphene layers. Similar observations can be observed from the Table 3 which shows the SPR angle shifts as a function of MoS₂ layer thickness. This time, however, the SPR angle shift is a large as $\Delta\theta_{RES} = 0.43^\circ$ when the MoS₂ layer thickness is 5 layers. As a result, the shift in resonance angle improved by 87% when the background substrate was enhanced with 4 additional MoS₂ layers. Besides, the rising ratio in the

Number of layers	Ag-Thickness	Reflected Intensity	FWHM	θ_{RES}	θ_{RES}	$\Delta\theta_{RES}$
Graphene	(nm)	(arb. unit)		w/o ssDNA	with ssDNA	
0	55	$\sim 92 \times 10^{-5}$	0.4258°	52.04°	52.23°	0.19°
Background	44	$\sim 22 \times 10^{-5}$	1.4739°	52.91°	53.14°	0.23°
2	41	$\sim 64 \times 10^{-5}$	1.9454°	53.11°	53.35°	0.24°
3	40	$\sim 9.3 \times 10^{-5}$	2.3003°	53.30°	53.54°	0.24°
4	38	$\sim 10 \times 10^{-5}$	2.8402°	53.51°	53.76°	0.25°
5	37	$\sim 5.6 \times 10^{-5}$	3.3122°	53.72°	53.98°	0.26°

Table 2: **Enrichment with Graphene**

Number of layers	Ag-Thickness	Reflected Intensity	FWHM	θ_{RES}	θ_{RES}	$\Delta\theta_{RES}$
MoS ₂	(nm)	(arb. unit)		w/o ssDNA	with ssDNA	
0	55	$\sim 92 \times 10^{-5}$	0.4258°	52.04°	52.23°	0.19°
Background	44	$\sim 22 \times 10^{-5}$	1.4739°	52.91°	53.14°	0.23°
2	40	$\sim 30 \times 10^{-5}$	2.7203°	53.80°	54.07°	0.27°
3	37	$\sim 40 \times 10^{-5}$	4.7312°	54.94°	55.25°	0.31°
4	34	$\sim 18 \times 10^{-5}$	8.3131°	56.43°	56.79°	0.36°
5	32	$\sim 0.8 \times 10^{-5}$	13.5693°	58.34°	58.77°	0.43°

Table 3: **Enrichment with MoS₂**

resonance angle without ssDNA is a constant, in the level of 0.2° per graphene layer, and it implies this ratio doesn't depend on the thickness of the metal substrate. In this regard, the resonant angle shift related to the background structure was evaluated with respect to the varied thickness of the metal, and it was observed $\Delta\theta_{RES}$ was stable and constantly equaled to 0.23° (supplementary information). However, the metal layer thickness may has a large effect on the reflected light intensity (and thus the surface plasmons' amplitude) which is consistent with the results reported by [48].

Furthermore, keeping everything the same, except replacing the SF11 prism with a BK7 glass prism ($n = 1.5151$), the model was modified. The resonance angle shift of the biosensor with the BK7 glass prism improved about 11% for 5 layers graphene, which is less than the result of the initial model. It was also observed that the drop in the refractive index of the prism made the SPR curves more wider and increased FWHM parameter. Equation (3) states that the resonance angle depends on the optical properties of the first medium, i.e. the prism. Therefore, it seems to be the case that SF11 glass is better than BK7 glass for the proposed hybrid structures.

3.2. The Sensitivity of the Proposed Biosensors

The major performance parameter of an SPR biosensor is the sensitivity, and the change in resonance angle determines the angular sensitivity, which is given by:

$$Sensitivity(S) = \frac{\Delta\theta_{RES}}{\Delta n} \quad [deg/RIU] \quad (13)$$

where Δn is the change in the refractive index due to biomolecules. Considering the cases of low biomolecule concentration and the inhomogeneity in the sample, sensitivity investigation was performed for 3.2 nm ssDNA

layer instead of conventional relatively large number of biomolecule thickness approach. The sensitivity improved by 21% when the pure Ag conventional sensor was coated with MoS₂/graphene bilayer. Sensitivity comparison in Fig. 5 reveals that this parameter increases monotonically with the number of atomic layers for both, MoS₂ or graphene sensors opposite to the results of the simulations performed for gold (Au)-silicon (Si) substrate in a recent study [39]. Moreover, the nonzero imaginary part of MoS₂'s permittivity is bigger than that of graphene, and this term refers to the electron energy loss and the attenuation of surface plasmons. The rise in the sensitivity is greater in case of MoS₂ than that of graphene which may create such an impression that there is no a direct proportion between the intensity enhancement (at the interface of graphene-MoS₂-metal hybrid substrate-adjacent layer) and the angular sensitivity. However, another performance parameter, namely, the detectability must also be taken into account, which is basically evaluated within the intensity enhancement, i.e. the sensor power. Even though an extensive detectability analysis is out of the context in this work, the intensity enhancement is considered during the investigation. The biosensor performance was also examined for large number of atomic layers. The rise in the sensitivity goes on for 8 layers in case of MoS₂, and then it begins to drop. Graphene still provides enhancement to sensor performance even for 20 layers. However, the fabrication of a sensor structure with the large number of atomic layers is difficult at the moment. In addition, electrical field enhancement factor (EFEF), refers to the ratio between the maximum and the average electric field at the surface, is dropped slightly bigger than half when the background is coated with 4 additional MoS₂, as shown in Fig. 6. Therefore, the number of atomic layers can be used for enhancement is determined as 5.

Figure 4: SPR spectra of the biosensors (a) with 37 nm thickness Ag-film with respect to the the number of graphene (b) with 32 nm thickness Ag-film with respect to the the number of MoS₂.

Same simulations were also performed in case of 10 times thicker ssDNA ($d_5 = 32nm$). In this case, the shift in resonance angle for the background structure takes the value of 2.3° instead of 0.23°, and rises in a same manner for both MoS₂ or graphene enrichment. This phenomenon can also be seen in Fig. 7, the change in resonance angle shift to the refractive index of the sensing medium. Fig. 7 shows that all calibration curves are linear, and 1L graphene–5L MoS₂–metal (32nm) hybrid structure provides the thinnest design and the better sensing performance than both metal and graphene based approaches, in particular the sensitivity improvement of this design is 2.3 times larger than that of pure metal sensor.

3.3. The Origin of the Biosensor Sensitivity and the Equivalent Permittivity

The origin of the improved biosensor sensitivity can be explained by studying equation (3). The argument of sine, i.e. θ_{RES} , in equation (3) just depends on the permittivities of both the metal (ϵ_m) and adjacent media (ϵ_a) in

Figure 5: Variation of sensitivity with respect to the the number of graphene and MoS₂ layers.

case of other parameters ϵ_p and λ are constant. Note that ϵ_a represents indeed an equivalent permittivity of MoS₂-graphene heterostructure within the analyte medium. As shown in Fig. 4, the resonance angle shifts with the number of either graphene or MoS₂, and this change simply and only can come from a variation in ϵ_a according to equation (3). This outcome proves that optical properties of a multilayered structure also depend on the thickness of layers. Hence, ϵ_a can be defined by a combination of the thicknesses and the permittivities of the related layers. In addition, the resonance condition (3) of the classical Kretschmann's configuration (also for Otto's configuration) needs to be reformed in such a way that involving not only permittivities, but also the thicknesses of the all layers. Moreover, Fig. 4(a-b) show that MoS₂ ($\sim 0.65nm$ thickness) produces bigger shift in the resonance angle than that of graphene ($\sim 0.34nm$ thickness) which means the relatively thicker materials are dominant in the optical properties of a multilayered structure. On the other hand, MoS₂ has a higher real part of the permittivity than graphene and this is the another reason of the greater rise in the sensitivity in case of MoS₂. Therefore, to obtain the largest sensitivity improvement, a material with a small imaginary (loss) but also a large real part in permittivity is needed and of all those possible materials MoS₂ is a promising candidate. Note that equation (3) indicates an ideal case and doesn't reflect the effects of ϵ_a on the speed of light. In practice, however, we expect larger improvements in sensitivity due to smaller electromagnetic wave speed in MoS₂.

Figure 6: Electrical field enhancement factor

Figure 7: Resonance angle shift in conventional metal, background, Ag-1L MoS₂-5L graphene and Ag-5L MoS₂-1L graphene biosensors. The thickness of each structure is 55 nm, 44 nm, 37 nm and 32 nm, respectively. The refractive index is varied by $\Delta n_{bio} = 0.005$.

4. Conclusion

In this work, we demonstrated the sensitivity of graphene-MoS₂-metal hybrid structure based plasmonic biosensors can be highly improved by a few number of MoS₂ layer within the angular detection. Our results show that the sensitivity of the background structure can be improved by 87% and 13% with the 4 additional MoS₂ and graphene layers, respectively, and it can be ~ 2.3 times as large, when the metal substrate is coated with 5 layer MoS₂ and 1 layer graphene. We prove with the proposed model, the metal thickness doesn't effect the angular sensitivity, and it can be reduced significantly (from 55 nm to 32 nm) while increasing the sensitivity. Angular detection scheme is a simple measurement setup (in contrast to phase detection), and our results provide the basic results to produce highly sensitive angular detection based portable devices in the near future. We show that the equivalent optical properties (refractive index, the permittivity) also depend on the layer thickness in a multilayered system. In this regard, we present here also a new approach for further investigations on other SPR based plasmonic devices based on a multilayered system.

Acknowledgements

The authors acknowledge the funding (1059B191501011) from Scientific and Technological Research Council of Turkey (TUBITAK).

Appendix A. Supplementary data

Supplementary data can be found at..

References

- Ozbay, E.. Review plasmonics: Merging photonics and electronics at nanoscale dimensions. *Science* 2006;311(5758):189–193.
- Pitarke, J.M., Silkin, V.M., Chulkov, E.V., Echenique, P.M.. Theory of surface plasmons and surface-plasmon polaritons. *Rep Prog Phys* 2006;70(1):1–87.
- Jussila, H., Yang, H., Granqvist, N., Sun, Z.. Surface plasmon resonance for characterization of large-area atomic-layer graphene film. *Optica* 2016;3(2):151–158.
- Sadowski, J.W., Korhonen, I.K., Peltonen, J.P.. Characterization of thin films and their structures in surface plasmon resonance measurements. *Opt Eng* 1995;34(9):2581–2586.
- Tabassum, R., Mishra, S.K., Gupta, B.D.. Surface plasmon resonance-based fiber optic hydrogen sulphide gas sensor utilizing Cu-ZnO thin films. *Phys Chem Chem Phys* 2013;15:11868–11874.
- Wong, C.L., Olivo, M.. Surface plasmon resonance imaging sensors: A review. *Plasmonics* 2014;9(4):809–824.
- Homola, J.. Present and future of surface plasmon resonance biosensors. *Anal Bioanal Chem* 2003;377:528–539.
- Zeng, S., Baillargeat, D., Ho, H.P., Yong, K.T.. Nanomaterials enhanced surface plasmon resonance for biological and chemical sensing applications. *Chem Soc Rev* 2014;43(3426–3452).
- Piliarik, M., Homola, J.. Surface plasmon resonance (SPR) sensors: approaching their limits? *Optics Express* 2009;17(19):16505–16517.
- Chamtouri, M., Sarkar, M., Moreau, J., Besbes, M., Ghalila, H., Canva, M.. Field enhancement and target localization impact on the biosensitivity of nanostructured plasmonic sensors. *J Opt Soc Am B* 2014;31(5):1223–1231.
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Zhang, Y., Dubonos, S.V., et al., . Electric field effect in atomically thin carbon films. *Science* 2004;306:666–669.
- Nair, R.R., Blake, P., Grigorenko, A.N., Novoselov, K.S., Booth, T.J., Stauber, T., et al., . Fine structure constant defines visual transparency of graphene. *Science* 2008;320(5881):1308.
- Balandin, A.A., Ghosh, S., Bao, W., Calizo, I., Teweldebrhan,

- D., Miao, F., Lau, C.N.. Superior thermal conductivity of single-layer graphene. *Nano Lett* 2008;8(3):902–907.
- 420 14. Ferrari, A.C., Bonaccorso, F., Fal'ko, V., Novoselov, K.S., Roche, S., Bøggild, P., et al., . Science and technology roadmap for graphene, related two-dimensional crystals, and hybrid systems. *Nanoscale* 2015;7:4598–4810.
- 425 15. Sun, Z., Martinez, A., Wang, F.. Optical modulators with 2d layered materials. *Nano Photonics* 2016;10:227–238.
16. Song, B., Li, D., Qi, W., Elstner, M., Fan, C., Fang, H.. Graphene on au(111): A highly conductive material with excellent adsorption properties for high-resolution bio/nanodetection and identification. *ChemPhysChem* 2010;11(3):585–589.
- 430 17. Niu, J., Shin, Y.J., Ahn, Y.L.J.H., Yang, H.. Graphene induced tunability of the surface plasmon resonance. *Appl Phys Lett* 2012;100:061116.
18. Salihoglu, O., Balci, S., Kocabas, C.. Plasmon-polaritons on graphene-metal surface and their use in biosensors. *Appl Phys* 2012;100:213110.
- 435 19. Subramanian, P., Lesniewski, A., Kaminska, I., Vlandas, A., Vasilescu, A., Jonsson, J.N., et al., . Lysozyme detection on aptamer functionalized graphene-coated spr interfaces. *Biosensors and Bioelectronics* 2013;50:239–243.
- 440 20. Mohanty, G., Akhtar, J., Sahoo, B.K.. Effect of semiconductor on sensitivity of a graphene-based surface plasmon resonance biosensor. *Plasmonics* 2016;11:189–196.
21. Sreekanth, K.V., Zeng, S., Yong, K.T., Yu, T.. Sensitivity enhanced biosensor using graphene-based one-dimensional photonic crystal. *Sens Actuator B-Chem* 2013;182:424–428.
- 445 22. Wu, L., Chu, H.S., Koh, W.S., Li, E.P.. Highly sensitive graphene biosensors based on surface plasmon resonance. *Optical Express* 2010;18(14):14395.
23. Choi, S.H., Kim, Y.L., Byun, K.M.. Graphene-on-silver substrates for sensitive surface plasmon resonance imaging biosensors. *Optical Express* 2011;19(2):458–466.
- 450 24. Kalantar-zadeh, K., Ou, J.Z., Daeneke, T., Strano, M.S., Pumera, M., Gras, S.L.. Two-dimensional transition metal dichalcogenides in biosystems. *Advanced Functional Materials* 2015;25(32):5086–5099.
- 455 25. Novoselov, K.S., Jiang, D., Schedin, F., Booth, T.J., Khotkevich, V.V., Morozov, S.V., Geim, A.K.. Two-dimensional atomic crystals. *PNAS* 2005;102(30):10452.
26. Lee, Y.H., Zhang, X.Q., Zhang, W., Chang, M.T., Lin, C.T., Chang, K.D., et al., . Synthesis of large-area mos2 atomic layers with cvd. *Advanced Materials* 2012;24(17):2320.
- 460 27. Wu, H., Yang, R., Song, B., Han, Q., Li, J., Fang, Y.Z.Y., et al., . Biocompatible inorganic fullerene-like molybdenum disulfide nanoparticles produced by pulsed laser ablation in water. *ACS Nano* 2011;5(2):1276–1281.
- 465 28. Zhu, C., Zeng, Z., Li, H., Li, F., Fan, C., Zhang, H.. Single layer mos2 based nanoprobe for homogeneous detection of biomolecules. *J Am Chem Soc* 2013;135:5998–6001.
29. Sarkar, D., Liu, W., Xie, X., Anselmo, A.C., Mitragotri, S., Banerjee, K.. Mos2 field-effect transistor for next-generation label-free biosensors. *ACS Nano* 2014;8(4):3992–4003.
- 470 30. Kalantar-zadeh, K., Ou, J.Z.. Biosensors based on two-dimensional mos2. *ACS Sens* 2016;1(1):5–16.
31. Perkins, F.K., Friedman, A.L., Cobas, E., Campbell, P.M., Jernigan, G.G., Jonker, B.T.. Chemical vapor sensing with monolayer mos2. *Nano Lett* 2013;13:668–673.
- 475 32. Li, H., Yin, Z., He, Q., Li, H., Huang, X., Lu, G., et al., . Fabrication of single- and multilayer mos2 film-based field-effect transistors for sensing no at room temperature. *Small* 2012;8:63–67.
33. Geim, A.K., Grigorieva, I.V.. Van der waals heterostructures. *Nature* 2013;499:419–425.
34. Loan, P.T.K., Zhang, W., Lin, C.T., Wei, K.H., Li, L.J., Chen, C.H.. Graphene-mos2 heterostructures for ultrasensitive detection of dna hybridisation. *Advanced Materials* 2014;26(28):4838–4844.
- 485 35. Roy, K., Padmanabhan, M., Goswami, S., Sai, T.P., Ramalingam, G., Raghavan, S., Ghosh, A.. Graphene-mos2 hybrid structures for multifunctional photoresponsive memory devices. *Nat Nanotechnol* 2012;8:826–830.
36. Zeng, S., Hu, S., Xia, J., Anderson, T., Dinh, X.Q., Meng, X.M., Coquet, P., Yong, K.T.. Graphene-mos2 hybrid nanostructures enhanced surface plasmon resonance biosensors. *Sens Actuator B-Chem* 2015;207:801–810.
37. Kashif, M., Bakar, A.A.A., Arsad, N., Shaari, S.. Development of phase detection schemes based on surface plasmon resonance using interferometry. *Sensors* 2104;14:15914–15938.
38. Mishra, A.K., Mishra, S.K., Verma, R.K.. Graphene and beyond graphene mos2: A new window in surface-plasmon-resonance-based fiber optic sensing. *J Phys Chem C* 2016;120(5):2893–2900.
39. Maurya, J.B., Prajapati, Y.K., Singh, V., Saini, J.P., Tripathi, R.. Improved performance of the surface plasmon resonance biosensor based on graphene or mos2 using silicon. *Opt Commun* 2016;359:426–434.
40. Mak, K.F., Lee, C., Hone, J., Shan, H., Heinz, T.F.. Atomically thin mos2: A new direct-gap semiconductor. *Phys Rev Lett* 2010;105:136805.
41. Li, Y., Chernikov, A., Zhang, X., Rigosi, A., Hill, H.M., et al., . Measurement of the optical dielectric function of monolayer transition-metal dichalcogenides: Mos2, mose2, ws2, and wse2. *Phys Rev B* 2014;90:205422.
42. Gomez, A.C., Agrait, N., Bollinger, G.R.. Optical identification of atomically thin dichalcogenide crystals. *Appl Phys Lett* 2010;96(21):213116.
43. Bruna, M., Borini, S.. Optical constants of graphene layers in the visible range. *Appl Phys Lett* 2009;94(3):031901.
44. Johnson, P.B., Christy, R.W.. Optical constants of the noble metals. *Phys Rev B* 1972;6(12):4370–4379.
45. Gray, D.E., Case-Green, S.C., Fell, T.S., Dobson, P.J., Southern, E.M.. Ellipsometric and interferometric characterization of dna probes immobilized on a combinatorial array. *Langmuir* 1997;13(10):2833–2842.
46. Jackson, J.D.. Classical Electrodynamics. 3rd ed.; Wiley; 1998.
47. Hansen, W.N.. Electric fields produced by the propagation of plane coherent electromagnetic radiation in a stratified medium. *J Opt Soc Am* 1986;58(3):380–390.
48. Ekgsit, S., Thammacharoen, C., Yu, F., Knoll, W.. Influence of the metal film thickness on the sensitivity of surface plasmon resonance biosensors. *Appl Spectrosc* 2005;59(5):661–667.