

Highly sensitive graphene biosensors based on surface plasmon resonance

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Abstract: A surface plasmon resonance (SPR) based graphene biosensor is presented. It consists of a graphene sheet coated above a gold thin film, which has been proposed and experimentally fabricated recently [ChemPhysChem 11, 585 (2010)]. The biosensor uses attenuated total reflection (ATR) method to detect the refractive index change near the sensor surface, which is due to the adsorption of biomolecules. Our calculations show that the proposed graphene-on-gold SPR biosensor (with L graphene layers) is $(1 + 0.025 L) \times \gamma$ (where $\gamma > 1$) times more sensitive than the conventional gold thin film SPR biosensor. The improved sensitivity is due to increased adsorption of biomolecules on graphene (represented by the factor γ) and the optical property of graphene.

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Surface plasmon resonance (SPR) biosensors are optical sensors, which use surface plasmon polariton waves to probe the interactions between biomolecules and the sensor surface. A surface plasmon polariton (SPP) is a perpendicularly confined evanescent electromagnetic wave, which propagates at the interface between a metal and a dielectric (i.e. sensing medium) [1]. In the sensing medium, a change in biomolecules concentration will produce a local change in the refractive index (RI) near the metal surface. The RI change will in turn lead to a change in the propagation constant of SPP, which can be optically measured by attenuated total reflection (ATR) method [2].

In the conventional SPR biosensor configuration, a thin metallic film is coated on one side of the prism, separating the sensing medium and the prism. The metallic film is typically made from noble metals, such as gold [1–3] and silver [4–6], which support the propagation of surface plasmon polariton at visible light frequencies. But, gold is usually preferred because it has good resistance to oxidation and corrosion in different environments. However, biomolecules adsorb poorly on gold. This drawback limits the sensitivity of the conventional SPR biosensor. Over the past two decades, surface plasmon resonance biosensor technology has made a tremendous growth and several strategies which utilize metal nanoparticles and nanoholes [7, 8], metallic nanoslits [9], and colloidal gold nanoparticles in buffered solution [10], have been proposed in order to improve the sensitivity of the biosensor. However, the precise control over the geometry and the optical properties of nanostructures is challenging.

Another attractive alternative to improve the sensitivity of SPR biosensor is to functionalize the gold film with biomolecular recognition elements (BRE) in order to enhance the adsorption of biomolecules on the gold surface [11]. In this study, we propose to use graphene as the BRE, where a sheet of graphene is coated on the gold surface in the conventional SPR biosensor setup. Graphene-on-Au (111) has been proposed and fabricated very recently, which is shown to stably adsorb biomolecules with carbon-based ring structures (e.g. ssDNA) [12]. This special property of graphene enables a greater refractive index change near the graphene | sensing medium interface than that of the conventional SPR biosensor. Moreover, the coating of the gold surface with graphene will also modify the propagation constant of surface plasmon polariton (SPP); thereby change the sensitivity to refractive index change. Thus in this paper, we take into account the BRE feature and the optical influence of graphene on conventional gold thin film SPR biosensor. We will show that our proposed graphene SPR biosensor will be substantially more sensitive than the conventional SPR biosensor.

To assess the sensitivity of the graphene based optical sensor, it is necessary to know the optical property of graphene. A recent experimental measurement [13] on light transmission through suspended graphene membranes showed that graphene opacity is a universal constant (independent of the wavelength). Based on the measurement, the dielectric function $\epsilon(\lambda_0)$ or the complex refractive index $n(\lambda_0)$ of graphene in the visible range was obtained within the framework of Fresnel coefficients calculation [14]:

$$n = 3.0 + i \frac{C_1}{3} \lambda_0, \quad (1)$$

where the constant $C_1 \approx 5.446 \mu\text{m}^{-1}$ is implied by the opacity measurement by Nair [13], and λ_0 is the vacuum wavelength. To validate its applicability, we performed full wave electromagnetic field simulation in frequency domain using CST MICROWAVE STUDIO®2009 [15]. In the simulation, graphene of thickness $d = L \times 0.34 \text{ nm}$ [14, 16] (where L is the number of graphene layers) is sandwiched between two vacuum blocks.

In Fig. 1, we show the simulated (crosses) and measured (squares) [13] light transmittance as a function of the number of graphene layers. Consistent with experimental results, the light

transmittance through monolayer graphene is about 97.7%, which is related to the fine structure constant α by $\pi\alpha = 2.3\%$ [13]. It implies that a one-atom-thick graphene layer will absorb 2.3% of incident light. The simulated transmittance is also found to decrease with increasing graphene thickness, and each additional graphene layer absorbs another 2.3%. The consistency of our simulation results with the measured optical spectra enables us to use this complex refractive index to predict the optical behavior of graphene for surface plasmon resonance biosensing.

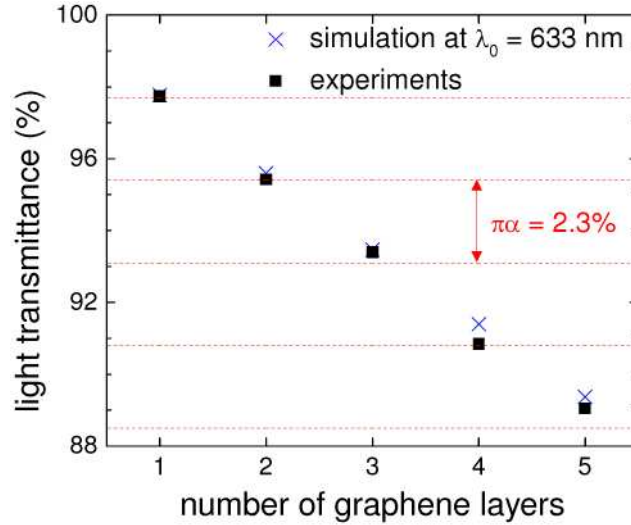


Fig. 1. Simulated transmittance of light at $\lambda_0 = 633$ nm (crosses) and measured transmittance of white light (squares) [13] as a function of the number of graphene layers. The dashed lines correspond to an intensity reduction by $\pi\alpha = 2.3\%$ with each added layer, where α is the fine structure constant [13].

Figure 2 shows the configuration of the proposed graphene-on-gold surface plasmon resonance biosensor, where the gold surface is covered with a SF10 glass prism. A light wave (of vacuum wavelength λ_0) passes through the prism and is totally reflected at the prism-metal interface, generating an evanescent wave. This evanescent wave can penetrate the thin gold layer (50 nm) and propagate along the x direction with propagation

constant $k_x = n_{prism} \left(\frac{2\pi}{\lambda_0} \right) \sin \theta$. The propagation constant k_x can be adjusted to match that of

the surface plasmon polariton (SPP) by controlling the angle of incidence θ . The interaction of the light wave and the SPP can change the characteristics of light wave, such as the totally reflected intensity R . The plot of totally reflected intensity versus angle of incidence is called surface plasmon resonance (SPR) curve.

To generate a SPR curve, we will use a generalized N-layer model as shown in Fig. 2. The total reflection of the N-layer system for a transverse-magnetic wave is [17]

$$R = \frac{\left| (M_{11} + M_{12}q_N)q_1 - (M_{21} + M_{22}q_N) \right|^2}{\left| (M_{11} + M_{12}q_N)q_1 + (M_{21} + M_{22}q_N) \right|^2}, \quad (2)$$

$$M_{ij} = \left(\prod_{k=2}^{N-1} M_k \right)_{ij}, \quad i, j = 1, 2, \quad (3)$$

and

$$M_k = \begin{bmatrix} \cos \beta_k & -i \sin \beta_k / q_k \\ -i q_k \sin \beta_k & \cos \beta_k \end{bmatrix}, \quad (4)$$

$$q_k = \frac{(\epsilon_k - n_1^2 \sin^2 \theta)^{1/2}}{\epsilon_k}, \quad (5)$$

$$\beta_k = d_k \left(\frac{2\pi}{\lambda_0} \right) (\epsilon_k - n_1^2 \sin^2 \theta)^{1/2}. \quad (6)$$

Here, the first layer is prism with refractive index $n_1 = n_{\text{prism}}$. The k^{th} layer (k is from 2 to $N - 1$) has a thickness of d_k and the local dielectric function $\epsilon(\lambda_0)$ or the refractive index $n(\lambda_0)$. In this study, we will focus on the following system for He-Ne laser light ($\lambda_0 = 633$ nm): prism ($n_1 = 1.723$) | Au ($d_2 = 50$ nm, $n_2 = 0.1726 + i 3.4218$) | graphene ($d_3 = L \times 0.34$ nm, $n_3 = 3 + i 1.149106$) | water ($n_4 = 1.33$), where L is the number of graphene layers. The biomolecular recognition element - graphene will absorb the biomolecules (e.g. ssDNA of size $z_0 = 100$ nm [18]) present in the water, and produce a local increase in the refractive index Δn at the graphene surface ($0 < z < z_0$).

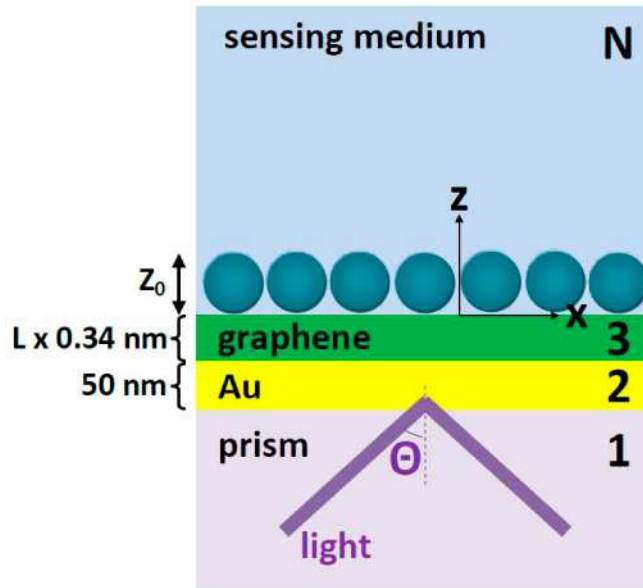


Fig. 2. The N-Layer model for surface plasmon resonance (SPR) biosensor: prism | Au (50 nm) | graphene ($L \times 0.34$ nm) | sensing medium, where L is the number of graphene layers, and $z_0 = 100$ nm is the thickness of biomolecule layer.

The sensitivity of the biosensor S is defined as the ratio of the change in sensor output P , e.g. angle of incidence, to the change in measurand, e.g. moles of biomolecules, M [11]:

$$S^L = \frac{\Delta P^L}{\Delta M} = \frac{\Delta P^L}{\Delta n} \cdot \frac{\Delta n}{\Delta M} = S_{RI}^L \cdot E \quad (7)$$

for different number of graphene layers L . The overall sensitivity S_L consists of two components: (i) the sensitivity to refractive index change $S_{RI}^L = \frac{\Delta P^L}{\Delta n}$ and (ii) the efficiency $E = \frac{\Delta n}{\Delta M}$. The second term E represents the adsorption efficiency of the target

biomolecule on the biomolecular recognition element, i.e., how many percent of biomolecules in the water can be adsorbed and converted into the change in the refractive index. Compared to the gold surface, the graphene adsorbs biomolecules more strongly and stably [12], due to the π -stacking interactions [19, 20] between graphene's hexagonal cells and the carbon-based ring structures in biomolecules. Therefore the enhanced adsorption efficiency $E_{\text{graphene}} = \gamma E_{\text{conventional}}$ (where $\gamma > 1$) is one of the important mechanisms to increase the overall sensitivity. Note that the exact value of γ requires experimental measurement.

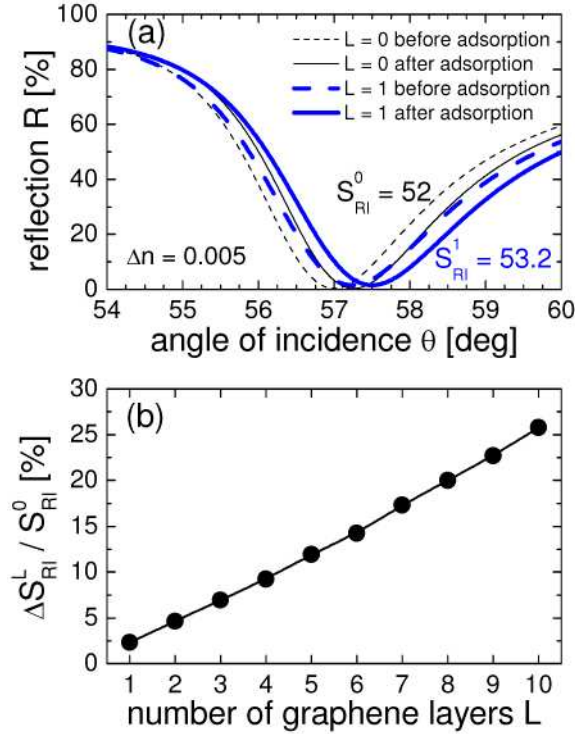


Fig. 3. (a) The surface plasmon resonance curves for the conventional biosensor ($L = 0$) (black thin lines) and the monolayer graphene biosensor ($L = 1$) (blue thick lines) for He-Ne laser light ($\lambda_0 = 633$ nm): prism (1.723) | Au (50 nm, $0.1726 + i 3.4218$) | graphene ($L \times 0.34$ nm, $3 + i 1.149106$) | water (1.33) before (dashed lines) and after (solid lines) the adsorption of biomolecules, assuming the same refractive index change $\Delta n = 0.005$. (b) The sensitivity enhancement $\Delta S_{\text{RI}}^L / S_{\text{RI}}^0$ as a function of the number of graphene layers L .

In addition to the increased adsorption efficiency E , the coating of the graphene sheet can also increase the sensitivity to refractive index change S_{RI}^L . Based on the N-layer model, we calculate and show the surface plasmon resonance (SPR) curves in Fig. 3(a) for the conventional biosensor ($L = 0$) (black thin lines) and the monolayer graphene biosensor ($L = 1$) (blue thick lines) before (dashed lines) and after (solid lines) the adsorption of biomolecules, assuming the same refractive index change $\Delta n = 0.005$. For each SPR curve, at resonant condition, the excitation of surface plasmon polariton is recognized as a minimum in the totally reflected intensity R (i.e. ATR minimum). The angle of incidence at ATR minimum is called SPR angle. We observe that the adsorption of biomolecules will shift the SPR curve toward a larger SPR angle. For example, there is a SPR angle shift of $\Delta P^0 = 0.26$ and $S_{\text{RI}}^0 = 52$ for the conventional SPR biosensor, and a shift of $\Delta P^1 = 0.266$ and $S_{\text{RI}}^1 = 53.2$ for the monolayer graphene biosensor as indicated in Fig. 3(a). With reference to the conventional SPR biosensor S_{RI}^0 , we plot the sensitivity enhancement $\Delta S_{\text{RI}}^L = S_{\text{RI}}^L - S_{\text{RI}}^0$ as a function of the number of graphene layers L in Fig. 3(b). It is found that coating more graphene layers is able to provide an increased sensitivity. The sensitivity enhancement $\Delta S_{\text{RI}}^L / S_{\text{RI}}^0$ can be as high as 25% for $L = 10$. This improvement in sensitivity results from the

optical property of graphene. At $\lambda_0 = 633$ nm, the refractive index of graphene is $n_{\text{graphene}} = 3 + i 1.149106$, and the dielectric function of graphene is $\epsilon_{\text{graphene}} = 7.68 + i 6.89$. It means that graphene is a dielectric material at $\lambda_0 = 633$ nm. Coating of the gold surface with a dielectric film will change the power flow in the different layers and modify the field of the surface plasmon polariton (SPP) [2, 21]. In such a way, the position of the SPR angle, the depth and the width of the ATR minimum will change with increasing thickness of graphene. This modification to the SPR curves will indeed lead to an increased S_{RI} . However, it should be noted that adding more graphene layers will broaden the SPR curves, which may cause difficulties in a SPR measurement.

In summary, a surface plasmon resonance biosensor based on graphene-on-gold has been presented. Compared to the conventional gold thin film SPR biosensor, the addition of a few graphene layers is able to increase the sensitivity by $(1 + 0.025 L) \times \gamma$ times (where $\gamma > 1$). The increased sensitivity results from two properties of graphene: (a) graphene adsorbs biomolecules with carbon-based ring structures strongly and stably, so that graphene can be used as the biomolecular recognition element to enhance the adsorption efficiency E by a factor of γ ; (b) graphene's optical property modifies the SPR curves and increases the sensitivity to refractive index change S_{RI} by 25% for $L = 10$. This is to say, the overall sensitivity S will be increased 5 times if graphene adsorbs 4 times ($\gamma = 4$) more biomolecules; likewise, if $\gamma = 2$, S will be increased 2.5 times. As graphene-on-Au (111) has already been successfully demonstrated using transfer printing technique [12], the concept presented in this paper is expected to be realized easily.

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