



Article Theoretical Design of Near-Infrared Tunable Surface Plasmon Resonance Biosensors Based on Gate-Controlled Graphene Plasmons

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Abstract: A tunable near-infrared surface plasmon resonance (SPR) biosensor based on gate-controlled graphene plasmons is numerically investigated by using the finite element method (FEM) and the transfer matrix method (TMM). The novel properties of chemical potential sensing make the proposed sensor promising in the application of ultra-sensitive and highly specific biosensing technology. The sensitivity of chemical potential sensing in wavelength interrogation mode can be calculated to be 1.5, 1.89, 2.29, 3.21, 3.73 and 4.68 nm/meV, respectively, at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The figure of merit (FOM) achieves 129.3, 101.1, 84.5, 67.7, 69.5 and 59.7 eV^{-1} , respectively, at these resonance wavelengths. The sensitivity of chemical potential sensing in gate voltage interrogation mode also can be calculated to be 156.9822, 143.6147, 131.0779, 111.0351, 101.3415 and 90.6038 mV/meV, respectively, at the incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The FOM achieves 135.6, 103.0, 88.9, 62.2, 66.6 and 61.5 eV^{-1} , respectively, at these incident wavelengths. Theoretical estimates suggest that the limit of detection (LOD) of the sensor's DNA sensing can reach the level of femtomolar or even attomolar, comparable to and even lower than that of 2D nanomaterial-enhanced metal SPR sensors with AuNPs as a sensitivity enhancement strategy. The feasibility of preparation and operation of this new concept SPR biosensor is also analyzed and discussed.

Keywords: surface plasmon resonance biosensor; graphene plasmon; chemical potential sensing

1. Introduction

SPR biosensors are powerful optical sensors for probing interactions between an analyte in solution and a biomolecular recognition element immobilized on the SPR sensor surface. In noble metal-based SPR biosensors, a surface plasmon wave (SPW) that propagates along the surface of the metal can be excited by an incident light (through prism, waveguide-, or grating-coupling methods) if the component of its wave vector that is parallel to the metal surface matches that of the SPW [1]. When the target bio molecules (antigens, target DNAs, etc.) in the aqueous solution are captured by specific biomolecule recognition elements (antibodies, probe DNAs, etc.) immobilized on the SPR sensor surface, the binding-induced refractive index change in the analyte layer will cause the change of the propagation constant of SPW that propagates along the interface between the metal and the dielectric (analyte layer). The characteristics of a light wave, such as amplitude, phase, polarization, and spectral distribution, consequently change due to its interaction with the SPW. By measuring the change of one of the light wave characteristics (through angle, wavelength, intensity, phase, or polarization interrogation), the binding-induced refractive



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Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). index change can be determined. However, the weak adhesion between metal surfaces and biomolecule recognition elements limits the sensitivity of the SPR biological sensors. In the last decade, the use of graphene, black phosphorose (BP), transition metal dichalcogenides (TMDCs) and other 2D materials to enhance the performance of SPR biological sensors has attracted wide attention [2]. The enhancement of the sensitivity of 2D material-enhanced metal SPR sensors was demonstrated experimentally in protein detection [3–5], glucose detection [6], immunoassay [7,8], and DNA sensing [9–13]. Despite that the sensitivity of noble metal-based SPR sensors has been greatly improved by using various sensitization strategies, these sensors still have some inherent disadvantages to overcome: (1) The refractive index sensing property of a noble metal-based SPR sensor makes it easy to be interfered with and has poor specificity [1]. (2) Many 2D material-enhanced metal SPR biosensors still need to rely on the synergistic effect of the localized SPR effect of metallic nanoparticles [14] to achieve high sensitivity, which increases the complexity, expenditure, and uncertainty of the sensors. (3) In general, noble metal-based SPR sensors are not tunable.

Plasmons supported by graphene, a 2D semiconductor, have a different characteristic than those in noble metals: tunability by gating or doping [15,16]. In the early stages, graphene plasmons were studied mainly in the terahertz to mid-infrared waveband [17–22]. Based on the relation $\omega_p \propto (\mu_c/D)^{1/2}$, where ω_p , μ_c , and D represent the frequency of plasmon resonance in graphene nanostructure, the chemical potential (Fermi level) of graphene, and the characteristic dimension of graphene nanostructure, respectively, a potential way to extend graphene plasmon research to near-infrared and even visible bands is constantly reducing the size of the graphene nanostructure [23,24]. Until now, the shortest wavelength of incident light for exciting the localized graphene plasmon was observed at 2 µm in 18 nm-diameter graphene nanodisks [25]. However, the challenges this approach (further reduction in size) faces are more complex preparation processes, reduced carrier mobility (lower by ~10 times or more than those of large 2D graphene sheets) [26,27], and increased defects related to the formation of graphene nanostructure edges [25]. Graphene plasmons have strong spatial light confinement (two orders [28] to even four orders [29] of magnitude higher than metal plasmons). Moreover, graphene plasmons possess unique properties, such as being tunable by electric [17,19,20], magnetic [30,31] and light fields [32], and the existence of novel polarization modes [33,34]. These interesting properties of graphene plasmons have prompted people to begin to study the graphene surface plasmon resonance (GSPR) biosensors and expect them to overcome the shortcomings of noble metalbased SPR biosensors. Current research on GSPR biosensors has correspondingly focused on the mid-infrared to terahertz bands. This is because current technologies allow the width of graphene nanoribbons (or other shaped nanostructures) to be reduced to the point where they can excite plasma oscillations in the mid-infrared bands. A graphene nanoribbon array (GNA)-based tunable mid-infrared plasmonic biosensor was demonstrated experimentally for protein detection [28]. The theoretical study of a mid-infrared SPR biosensor based on a GNA and prism coupling system shows that it can realize sensitive refractive index sensing by scanning the chemical potential of graphene [35]. In additional to GNA, a mid-infrared graphene plasmon can also be excited through guided-wave resonance with a homogeneous graphene-on-silicon grating structure [36,37]. A terahertz graphene plasmon can be excited in a homogeneous graphene film with a high doping level by using a high index prism coupling system [38]. In the last few years, several prism-configuration THz GSPR sensors [39–41] have been theoretically investigated.

Inspired by the study of near-zero refractive index materials or structures [42–44], a new scheme (different from constantly reducing the size of the graphene nanostructure) for extending the energy of a graphene plasmon into a near-infrared spectrum window is adopted. In this paper, a near-infrared tunable GSPR biosensor consisting of a homogeneous graphene film heterojunction and a prism coupling system is proposed. In the heterojunction, if Si_3N_4 , which has a high dielectric constant (6.6, larger than 3.9 of SiO_2) and breakdown field (11.5 MV/cm) and also maintains good carrier mobility of the contacted graphene [45], is selected as a dielectric layer, the graphene can be adjusted to its

epsilon-near-zero (ENZ) point by the applied gate voltage. Graphene at or near its ENZ point can be excited; plasmon resonance occurs in it by near-infrared incident light due to the satisfaction of the momentum matching condition. In the wavelength range where the proposed sensor can work, that is, 1100–2000 nm, there are mature light sources and light detection instruments that have not yet been used for SPR sensing. The composition and optimization parameters of the sensor, sensing mechanism, sensitivity and FOM in the two sensing modes, and the influences of graphene quality and atomic layer number on the sensing performance are studied in this paper.

2. Sample Design and Numerical Method

The Kretschmann coupling configuration of the proposed sensor is shown in Figure 1. A 10 nm thick Au layer is deposited on the bottom of the prism. A 50 nm thick Si_3N_4 layer is sandwiched between the Au layer and a 5-atom-layer graphene film. The analyte layer is modeled as a uniform dielectric layer with a refractive index of n_a and thickness of 30 nm. The uppermost layer can be thought of as a semi-infinite aqueous solution with a refractive index of 1.33. The incident angle of the p-polarized light beam on the bottom of the prism is θ . Gate voltage between the Au layer and the graphene film as well as the attachment of bio molecules can exert the independent and superimposable doping effect on graphene [46]: the gate voltage can adjust the chemical potential (absolute value) in graphene to a suitable value (near ENZ point), causing the graphene to undergo plasmon resonance; the attachment of biomolecules can cause further changes in the chemical potential through charge transfer (or electrostatic gating), thereby shifting the resonance wavelength or resonance angle of the incident light.



Figure 1. Schematic diagram of the sensor.

Compared with the Otto prism coupling structure in our previous work [47], the Kretschmann configuration has the advantage of no restriction on the analyte layer thickness. The Au layer is adopted for playing the role of gating electrode. It can greatly reduce the difficulty of preparation compared with the structure of double graphene films separated by a dielectric layer. The Au layer can be deposited on a substrate that is homogeneous to the prism by using an e-beam evaporation method. The Si₃N₄ dielectric layer can be deposited on the Au layer by using a plasma-enhanced chemical vapor deposition (PECVD) method [45]. The multi-atom-layer graphene film can be prepared on the Si₃N₄ layer by using the standard wet transfer method to stack layers of single-atomic chemically vapor-deposited (CVD) graphene on top of each other [48]. The multi-atom-layer graphene film formed by this method allows the graphene layers to remain electrically interconnected

and can be simultaneously biased. When a gate voltage is applied, the injected charge carrier will be redistributed over multiple plasmonically coupled layers, which gives the multi-atom-layer graphene film a higher equivalent carrier density than the single-atom-layer graphene at the same gate voltage, and consequently gives the multi-atom-layer graphene film a higher equivalent chemical potential than the single-atom-layer graphene at the same gate voltage [49]. For simplicity, we assume that single- and multi-atom-layer graphene have the same chemical potential at the same gate voltage.

Resulting from the Kubo formula, the dynamic conductivity of graphene takes the following expression [50]:

$$\sigma(\omega,\mu_c,\Gamma,T) = \frac{ie^2k_BT}{\pi\hbar^2(\omega+i2\Gamma)} \Big[\frac{\mu_c}{k_BT} + 2\ln\Big(e^{-\mu_c/k_BT} + 1\Big) \Big] \\ + \frac{ie^2(\omega+i2\Gamma)}{\pi\hbar^2} \int_0^\infty \frac{f_d(-\varepsilon) - f_d(\varepsilon)}{(\omega+i2\Gamma)^2 - 4(\varepsilon/\hbar)^2} d\varepsilon$$
(1)

where ω , μ_c , Γ , T, i, e, k_B , ε and \hbar are angular frequency, chemical potential, scattering rate, temperature, imaginary unit, electron charge, Boltzmann's constant, energy and reduced Planck's constant, respectively. $f_d(\varepsilon) = \{1 + \exp[(\varepsilon - \mu_c)/k_B T]\}^{-1}$ is the Fermi–Dirac distribution. The relation between the relative permittivity ε_g (as well as the refractive index n_g) of graphene and its dynamic conductivity is [50]:

$$\varepsilon_g = n_g^2 = 1 + \frac{i\sigma}{\varepsilon_0 \omega t_g} \tag{2}$$

where ε_0 and $t_g = 0.34$ nm are the permittivity of vacuum and thickness of graphene, respectively. Calculated by using Equations (1) and (2), the function of $\varepsilon_g(\mu_c)$ under the condition of $\lambda = 1310$ nm, T = 298 K (room temperature) and $\Gamma = 1 \times 10^{12}$ Hz (when the scattering rate is equal to or below this value, graphene exhibits significant plasma absorption [51]) can be obtained, as shown in Figure 2a; the function of $\varepsilon_g(\lambda,\mu_c)$ under the condition of T = 298 K and $\Gamma = 1 \times 10^{12}$ Hz can also be obtained, as shown in Figure 2b,c. In this paper, for the convenience of narration, the chemical potential μ_{c0} corresponding to $|\varepsilon_g|$ approaching zero is referred to as the ENZ point, as shown in Figure 2a. Interestingly, in the near-infrared region, we have $\mu_{c0}(\omega) \approx 0.63\hbar\omega$, as shown in Figure 2b. Therefore, as frequency increases (wavelength decreases), μ_{c0} will increase, as shown in Figure 2c.

Although the Au layer is used as a back-gate electrode, its influence on the reflectance of the multilayer system should be taken into account. According the Drude model, the relative permittivity ε_{Au} of Au is equal to [52]:

$$\varepsilon_{Au} = 1 - \frac{\lambda^2 \lambda_c}{\lambda_p^2 (\lambda_c + i\lambda)} \tag{3}$$

where the plasma wavelength $\lambda_p = 1.6826 \times 10^{-7}$ m, and the collision wavelength $\lambda_c = 8.9342 \times 10^{-6}$ m.

The absolute refractive index of graphene at its ENZ point reaches the minimum value (close to zero), and the wave vector of the graphene plasmon can be greatly reduced to match that of the p-polarized incident light. So, the chemical potential required to trigger the plasmon resonance in graphene film (called the plasmon resonance point, PR point, labeled μ_{cPR}) should be found near the ENZ point, which can be implemented by using the 2D finite element method (FEM) in COMSOL. The FEM is an approximate numerical method to solve the mode field distribution in a waveguide structure by discretizing a continuous waveguide structure (or its cross-section) into a finite number of elements. Figure 3 displays the simulation model in COMSOL: the prism is assumed as a 5 μ m thick SiO₂ layer with refractive index of 1.45 (in part 3, the optimal material of the prism can be adopted in the 2D FEM simulation since it has been determined through TMM calculation in part 2); the analyte layer, together with the aqueous solution, is assumed as a 5 μ m thick layer with refractive index of 1.33; in between them are the 10 nm thick Au, 50 nm thick

 Si_3N_4 , and 1.7 nm thick graphene (5 atom layer). In order to guarantee the accuracy of the FEM simulation, the 1.7 nm thick graphene is divided into 3 layers; the cross-section of the multilayer system is meshed by free triangular meshing with the minimum element size of 0.1 nm and maximum element of 300 nm; the maximum element growth rate and the curvature factor are 1.1 and 0.2, respectively. The selection of such a waveguide cross-section size (width is 10 µm, height is also about 10 µm) ensures the accuracy of the calculation but does not make the calculation too time-consuming. The maximum element size is less than one-third of the incident wavelength, satisfying the criterion of FEM in COMSOL. The 2D FEM simulation is used to obtain the mode field distribution in the cross-section of the waveguide structure (prism-Au-Si₃N₄-graphene-analyte) through an iterative process. The refractive index of graphene (as a function of its chemical potential) is scanned to find the chemical potential value corresponding to the maximum mode field strength in the graphene layer, i.e., to find PR point.



Figure 2. (a) $\varepsilon_g - \mu_c$ relation curve under the conditions of $\lambda = 1310$ nm, T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz; (b) functional relation surface of $|\varepsilon_g| (\mu_c, \lambda)$ with μ_c in unit of $h\omega/2\pi$ under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz; (c) functional relation surface of $|\varepsilon_g| (\mu_c, \lambda)$ with μ_c in unit of eV under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz; (c) functional relation surface of $|\varepsilon_g| (\mu_c, \lambda)$ with μ_c in unit of eV under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz.

Table 1 lists ENZ points and PR points at different wavelengths. It can be found that $\mu_{cPR}(\lambda)$ increases with the reduction of resonance wavelength λ , and PR points are all greater than 0.3 eV in the near-infrared spectrum. So, generally speaking, near-infrared incident light cannot excite plasmon resonance in naturally doped graphene (since for naturally doped graphene, $|\mu_c| \leq 0.3$ eV [50]), not to mention the use of visible light to excite plasmon resonance in near-infrared spectrum. By applying the gate voltage, graphene's chemical potential can be adjusted to the PR points, so that the plasmon resonance in graphene can be excited by near-infrared incident light. The excitation required gate voltages can be obtained through the following formula [53]:

$$C(V_{DC} - V_{Dirac}) = en_s \tag{4}$$

and [54]

$$n_s = \frac{2}{\pi \hbar^2 v_F^2} \int_0^\infty \varepsilon [f_d(\varepsilon) - f_d(\varepsilon + 2\mu_c)] d\varepsilon$$
(5)

where V_{Dirac} is the voltage at the Dirac point, V_{DC} is applied DC gate field, $C = \varepsilon_0 \varepsilon_r / t$ is the gate capacitance (on unit graphene area), ε_r and t are relative permittivity and thickness of Si₃N₄ layer, respectively, and $v_F \approx 9.5 \times 10^5$ m/s [54] is the Fermi velocity. For undoped graphene, $V_{Dirac} = 0$, the required gate voltages (at incident wavelengths of 760, 850, 980, 1100, 1200, 1310, 1550, 1700, and 1900 nm, respectively) can be calculated and are also listed in Table 1. The breakdown field of Si₃N₄ is about 11.5 MV/cm [45], i.e., the breakdown voltage of 50 nm thick Si₃N₄ is about 57.5 V. Therefore, the sensor can operate in the wavelength range of $\lambda \ge 1100$ nm. If a thicker Si₃N₄ layer (thickness larger than 50 nm) is adopted, the breakdown voltage would increase, while the required gate voltages for trigging plasmon resonance in graphene would also increase in equal proportion. So, the permissible operating wavelength range is unchanged (i.e., still $\lambda \ge 1100$ nm).



Figure 3. 2D FEM simulation model in COMSOL.

Table 1. ENZ points, PR points, and required gate voltages for trigging plasmon resonance in graphene at different incident wavelengths.

Λ (nm)	760	850	980	1100	1200	1310	1550	1700	1900
μ_{c0} (eV)	1.037	0.923	0.798	0.709	0.649	0.594	0.502	0.458	0.410
μ_{cPR} (eV)	1.037	0.923	0.798	0.710	0.650	0.594	0.502	0.458	0.410
Vg (V)	119.6	94.8	70.9	56.2	47.1	39.4	28.2	23.5	18.9

Although the 2D FEM can find the PR point corresponding to a certain wavelength, the resonance angle of the beam incident at that wavelength, an important indicating or operating parameter in a prism coupling system, cannot be determined. TMM is a method based on the well-established Fresnel theory which can calculate the reflectance of p-polarized incident light in a multilayer system without approximations [2]. The resonance angle can be determined by studying the function relationship between reflectance and incident angle calculated by TMM. In order to select the optimal prism material of different wavelength incident light, several representative materials were considered: MgF_2 (1.37), CaF₂ (1.4261), ZBLAN (1.4688), BK7 (1.515), LF (1.575), Topaz (1.61), SF10 (1.723). The refractive index of the aqueous solution is set to 1.33, and the refractive index of the analyte layer is temporarily set to 1.33. The refractive index of Si_3N_4 in near-infrared spectrum can be taken as 2 [55,56]. The chemical potential in graphene film can be set to the corresponding PR points according to different incident wavelengths (see Table 1), and its refractive index can be calculated by using Equations (1) and (2) under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz. The refractive index of the Au layer is determined by Equation (3). The reflectance versus incident angle SPR curves of each monochromatic light

beam (wavelength 1100, 1200, 1310, 1550, 1700 and 1900 nm, respectively) for different prism materials were calculated, as shown in Figure 4. The first point of minimum reflectance in the curve from right to left indicates that a plasmon resonance occurs in graphene. The ordinate of this point can be labeled R_{min} , and the abscissa of the point is the resonance angle. When the incident wavelength is 1100 nm, R_{min} firstly decreases with the increase in the refractive index of the prism material, reaching the minimum value at LF (1.575), and then increases, as shown in Figure 4a. When the incident wavelength is 1200 nm, R_{min} firstly decreases with the increase in the refractive index of the prism material, reaching the minimum value at CaF₂ (1.4261), and then increases, as shown in Figure 4b. For the incident wavelengths of 1310, 1550, and 1700 nm, R_{min} values all reach the minimum value at MgF₂ (1.37), as shown in Figure 4c–e. For the incident wavelength of 1900 nm, the optimal prism material has a smaller refractive index than 1.37 (such as 1.35), as shown in Figure 4f. Here, we still take MgF₂ (1.37) as an optimal prism material for an incident wavelength of 1900 nm. It can be seen that the refractive index of the prism optimal material decreases as the wavelength of the incident light increases.



Figure 4. Reflectance versus incident angle SPR curves for different prism materials when using a monochromatic incident light beam with wavelengths of (**a**) 1100 nm; (**b**) 1200 nm; (**c**) 1310 nm; (**d**) 1550 nm; (**e**) 1700 nm; and (**f**) 1900 nm.

The optimal thickness of the Au layer t_{Au} is investigated by studying reflectance versus incident angle SPR curves. For different wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, by using the optimal prism material, namely, LF for 1100 nm, CaF₂ for 1200 nm, MgF₂ for 1310, 1550, 1700 and 1900 nm, respectively, the SPR curve under different gold film thicknesses t_a can be calculated. Figure 5 shows the situation when the incident wavelength is 1550 nm. It can be seen that R_{min} decreases with the decrease in the Au layer thickness. This is because more light energy can penetrate through the thinner Au layer and interact with the graphene. The SPR curves for other incident light wavelengths follow the same evolution law with changing the Au layer thickness, as in the case of 1550 nm. On the other hand, in order to ensure good electrical conductivity of the Au layer, its thickness should not be too small. By taking the optimal thickness of the Au layer to be 10 nm and adopting the optimal prism materials for different wavelengths, the



resonance angles can be obtained as 71.7°, 80.3°, 84.9°, 86.8°, 86.2° and 85.1° for different wavelength of 1100, 1200, 1310, 1550, 1700 and 1900 nm, respectively.

Figure 5. Reflectance versus incident angle SPR curves for different thickness of the Au layer when using a monochromatic incident light beam with a wavelength of 1550 nm.

The influence of the change in thickness of the Si_3N_4 layer on the optimal prism materials and corresponding resonance angles for different incident wavelengths is also investigated through angular interrogation method. The calculation results are placed in Appendix A. In the following sensing performance research, Si_3N_4 layer thickness is set as 50 nm.

The reflectance versus wavelength SPR curve with λ' (the value can be 1100, 1200, 1310, 1550, 1700 and 1900 nm, respectively) as the resonance wavelength can be calculated as follows: set the chemical potential of graphene to the corresponding PR point $\mu_{cPR}(\lambda')$; the refractive index of graphene $n_g(\lambda)$ as a function of λ (where λ forms a band around λ' , with λ' as the central wavelength) can be calculated by using Equations (1) and (2) under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz $\mu_c = \mu_{cPR}(\lambda')$; the optimal prism material is adopted, i.e., LF for 1100 nm, CaF₂ for 1200 nm, MgF₂ for 1310, 1550, 1700 and 1900 nm, respectively; the resonance angles of monochromatic incident beams with wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm calculated in the angular interrogation method, namely, 71.7°, 80.3°, 84.9°, 86.8°, 86.2° and 85.1°, are used as the incidence angles of broadband beams with these wavelengths as the resonance wavelength, respectively. The reflectance versus wavelength SPR curves at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, respectively, can be obtained by using TMM, as shown in Figure 6. The results show that the FWHM increases gradually with the increase in the resonance wavelength, and the FWHM at 1100, 1200, 1310, 1550, 1700 and 1900 nm is 11.6, 18.7, 27.1, 47.4, 53.7 and 78.4 nm, respectively. In contrast, the FWHM of the graphene oxide-Au SPR sensor whose resonance wavelength falls in the range of 600~900 nm is greater than 110 nm [4,5]. In general, FWHM increases with the increase in resonance wavelength. Therefore, it can be inferred that if the resonance wavelength of the 2D material-enhanced metal SPR sensor can reach the same near-infrared wavelengths (i.e., 1100~2000 nm), its FWHM is much larger than that of the proposed near-infrared GSPR sensor.



Figure 6. Reflectance versus wavelength SPR curve at the resonance wavelengths of (**a**) 1100 nm; (**b**) 1200 nm; (**c**) 1310 nm; (**d**) 1550 nm; (**e**) 1700 nm; (**f**) 1900 nm.

3. Results

3.1. Sensing Performance Based on Wavelength Interrogation Mode

Set the chemical potential of graphene film to PR point $\mu_{cPR}(\lambda')$ by applying gate voltage, and then the resonance wavelength would be λ' . When the target biomolecules in the aqueous solution are captured by specific biomolecule recognition elements immobilized on graphene, it causes a change in the refractive index of the analyte layer, while the chemical potential of graphene also changes due to the charge transfer (or electrostatic gating effect) between graphene and the attached target biomolecules. In order to estimate the response sensitivities of the resonance wavelength to the refractive index change in the analyte layer, i.e., refractive index sensitivity S_{RI} , defined by $S_{RI} = \Delta \lambda_{res} / \Delta n_a$, where $\Delta \lambda_{res}$ and Δn_a represent the resonance wavelength change and the refractive index change in the analyte layer, respectively, it is first assumed that the chemical potential of graphene film is not affected by the attached target biomolecules and remains at the PR point $\mu_{CPR}(\lambda')$, and the refractive index of the analyte layer is set to change within the range of 1.33~1.43. The refractive index of the uppermost layer of aqueous solution is set to 1.33. The evolution of SPR curves at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm with the refractive index change in the analyte layer can be obtained, as shown in Figure 7. The results show that the resonance wavelengths all shift very slightly (almost imperceptibly) to short wavelengths with the increase in the refractive index of the analyte layer. This is because a small part of the plasmon wave field enters the analyte layer through the graphene surface (see Figure 10b), and its transmission wave vector increases with the increase in the refractive index of the analyte layer. This results in a very slight reduction in the resonance wavelength to satisfy the momentum matching condition. The absolute RI sensitivity (S_{RI}) values are about 0, 0, 0, 50, 27 and 13 nm/RIU, respectively, at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm.



Figure 7. The evolution of SPR curves at resonance wavelengths of (**a**) 1100 nm; (**b**) 1200 nm; (**c**) 1310 nm; (**d**) 1550 nm; (**e**) 1700 nm; (**f**) 1900 nm, respectively, with the increase in the refractive index of the analyte layer.

In order to estimate the response sensitivities of the resonance wavelengths to the chemical potential change in graphene, which can be called chemical potential sensitivity (or CP sensitivity), the refractive index of graphene $n_g(\lambda)$ as a function of λ (where λ forms a band around λ' , with λ' as the central wavelength) can be calculated by using Equations (1) and (2) under the conditions of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz $\mu_c = \mu_{cPR}(\lambda') + \Delta \mu_c$, where $\Delta \mu_c$ represents the chemical potential shift from the PR point due to the attachment of analyte molecules. Assuming that the refractive index of the analyte layer (and the uppermost aqueous solution) is constant and set to 1.33, the evolution of SPR curves at resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, respectively, with the chemical potential change in the graphene film can be calculated, as shown in Figure 8. It can be seen that with the increase in chemical potential (absolute value) in graphene film, the resonance wavelengths all shift to smaller values (blue shift). This is because the greater absolute value of the chemical potential corresponds to the PR point of the shorter wavelength light (see Table 1). The CP sensitivity, labeled S_{CP}, defined as the ratio of the resonance wavelength change to the chemical potential change in the graphene film $\Delta \lambda_{res} / \Delta CP$, is about 1.5, 1.89, 2.29, 3.21, 3.73 and 4.68 nm/meV, respectively, at the resonance wavelength of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The CP sensitivity increases with the increase in the resonance wavelength, as shown in Figure 9a. The FOM for chemical potential sensing, defined as the ratio of the CP sensitivity to the FWHM, S_{CP}/FWHM, can also be calculated to be 129.3, 101.1, 84.5, 67.7, 69.5 and 59.7 eV^{-1} , respectively, at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700, and 1900 nm. Since the refractive index of graphene varies with its chemical potential, it is also possible to calculate the response sensitivity of the resonance wavelengths to the refractive index change in the graphene film (labeled S'_{RI} , defined as the ratio of the resonance wavelength change to the refractive index change in the graphene film, $\Delta \lambda_{res} / \Delta n_g$), and the values are 39.1, 43.8, 45.3, 61.4, 69.9 and 88.3 nm/RIU, respectively, at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, as shown in Figure 9b.



Figure 8. The evolution of SPR curves at the resonance wavelengths of (**a**) 1100; (**b**) 1200; (**c**) 1310; (**d**) 1550; (**e**) 1700; (**f**) 1900 nm, respectively, with the increase in chemical potential in graphene.



Figure 9. (a) CP sensitivities (S_{CP}) at different resonance wavelengths; (b) RI sensitivities (S'_{RI}) at different resonance wavelengths.

Obviously, either S_{RI} or S'_{RI} of the proposed near-infrared GSPR sensor is much lower than the RI sensitivity of the 2D material-enhanced metal SPR sensors, whose typical value is several thousands of nm/RIU [4,6], even more than ten thousand of nm/RIU [8]. The reason why the resonance wavelength is not sensitive to the refractive index change in the analyte layer may be that the plasmon is not on the surface of the graphene film, but inside the graphene film. This is because graphene at (or near) the ENZ point as an ENZ material achieves the same effect of mixing permittivity–positive material (such as dielectric analyte) and permittivity-negative material (such as metal) to bring the effective permittivity close to zero [43]. The concept of supercoupling is helpful to understand the distribution and propagation of plasmon wave energy inside the extremely thin 2D graphene film [43,44]. It is proved through the 2D FEM simulation that the plasmon mode field is almost completely distributed inside the graphene film, as shown in Figure 10. This is different from the case of a noble metal-based SPR sensor where plasmons exist at the interface between the metal and analyte, and are reduced exponentially in the metal and analyte [1]. For THz GSPR sensors [41] or mid-infrared GSPR sensors [36], the highly doped graphene acts as a metallic layer (not as an ENZ material), and the plasmon mode exists at the interface between the graphene and the analyte and decreases exponentially into the analyte. So, THz or mid-infrared GSPR sensors can also respond sensitively to the refractive index change in the analyte layer. For the proposed near-infrared GSPR sensor, the shift in resonance wavelength is directly caused by the chemical potential change in graphene due to the attachment of bio molecules and is almost independent of the binding-induced refractive index change in the analyte layer, so it should be considered to have a chemical potential sensing (rather than refractive index sensing) property.

This chemical potential sensing property can be used to sensitively detect analytes attached to graphene that cause significant changes in chemical potential. When charged biomolecules are adsorbed on chemically modified or biologically modified graphene surfaces, the chemical potential of graphene changes due to charge transfer [57] or the electrostatic gating effect [58]. Dong et al. found that hybridizing 0.01 nM complementary DNAs with probe DNAs pre-fixed to graphene resulted in a chemical potential shift of >10 meV in graphene [57]. For a proposed near-infrared GSPR sensor, a chemical potential shift of >10 meV in graphene would cause shifts of >15, >18.9, >22.9, >32.1, >37.3 and >46.8 nm, respectively, at resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The minimum detection limit of the sensor in biosensing is related to the resolution of the optical detection instrument. The wavelength resolution of a commonly used optical spectrum analyzer (OSA) (such as YOKOGAWA) can reach 0.02 nm in the near-infrared band. Therefore, suppose the proposed near-infrared GSPR sensor is used in the DNA sensing described in Ref. [57]; it can reach theoretical LOD of <13.33, <10.58, <8.73, <6.23, <5.36 and <4.27 fM, respectively, at the resonance wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. In contrast, the LOD of noble metal-based SPR sensors in DNA sensing is nM or sub-nM scale [59]. Although the LOD of the 2D material-enhanced metal SPR sensors in DNA sensing can reach fM or sub-fM scale, as shown in Table 2, they often require the use of gold nanostars (NS), nanoparticles (NP), or nanorods (NR) as sensitivity enhancement strategies, which increases the complexity, expenditure, and uncertainty of sensing performance.

SPR Structure	Theoretical/Experimental	LOD	FWHM	Ref.
HBAK1/Au film/graphene/AuNSs	experimental	0.5 fM	-	[9]
K9/Au film/graphene/AuNPs	experimental	0.5 fM	-	[10]
K9/Au film/antimonene/AuNRs	experimental	10 aM	-	[11]
K9/AuNT array/AuNPs	experimental	1.2 aM	114.471 nm	[12]
K9/Au film/GO-AuNPs	experimental	0.2 fM	-	[13]
MgF ₂ /Au film/Si ₃ N ₄ /graphene	theoretical	<4.27 fM	78.4 nm	this work
LF/Au film/Si ₃ N ₄ /graphene	theoretical	<21.66 aM	1158 mV	this work



Figure 10. (a) SPR curve at the resonance wavelength of 1310 nm obtained under the condition of $\theta = 84.9^{\circ}$, MgF₂ as prism material, $\mu_c = 0.594$ eV, the distributions of the electric field in the cross-section of the multilayer system corresponding to resonance and un-resonance wavelength are displayed in the left and right inset, respectively. The electric field intensity along the direction perpendicular to the prism interface for resonance wavelength (b) and un-resonance wavelength (c).

The chemical potential sensing property also gives the sensor another advantage: enhanced specificity. The charge carrier density (and therefore the chemical potential) of graphene can be changed by the attached biomolecules through two possible mechanisms: electrostatic gating or partial electron transfer [60]. For instance, negatively charged biomolecules can exert a p-doping effect on graphene through the electrostatic gating effect [58], or they can exert an n-doping effect on graphene through partial electron transfer caused by π -stacking interaction [57]. The p-doping and n-doping effects lead to an

increase and decrease in the absolute chemical potential of p-doped graphene, respectively (for n-doped graphene, the situation is reversed). Which of the two mechanisms plays a dominant role depends on the structure of the attached biomolecules. Inspecting the specificity of near-infrared GSPR sensors in DNA sensing will help us understand the advantages of chemical potential sensing over refractive index sensing. In DNA sensing, partial electron transfer mechanisms play a dominant role because the aromatic nucleotide bases in DNA are easily bound to graphene via π -stacking. For graphene film saturated with probe DNAs, specific binding between complimentary DNAs and probe DNAs prefixed to graphene (i.e., hybridization by hydrogen-bonds) produces an n-doping effect on the graphene, altering its chemical potential [57]; while mismatched DNA cannot be bound to graphene via π -stacking interactions (because graphene is saturated with probe DNAs), nor can it be bound to probe DNAs by hydrogen-bond interactions, so the non-specific attachment of mismatched DNAs to graphene has little doping effect on graphene and hardly changes the chemical potential of graphene [57]. As a result, near-infrared GSPR sensors based on chemical potential sensing can respond sensitively to the specific attachment of complimentary DNAs and have little to no response to non-specific attachment of mismatched DNAs, although their attachment to graphene may result in almost identical refractive index changes in the analyte layer.

3.2. Sensing Performance Based on Gate Voltage Interrogation Mode

In addition to wavelength interrogation mode, the sensor can also operate in gate voltage interrogation mode: i.e., detecting the change in the chemical potential of graphene by scanning the gate voltage provided by a high resolution digital-to-analog converter (DAC). The reflectance versus gate voltage SPR curve can be obtained through calculation as follows: according to the wavelength of monochromatic incident light beam λ' , the corresponding resonance angle $\theta(\lambda')$ (see Figure 6) is selected as the fixed incident angle; the chemical potential of graphene μ_c is set so that it varies around the corresponding PR point $\mu_{cPR}(\lambda')$ (see Table 1); the refractive index of graphene as a function of μ_c can be calculated by using Equations (1) and (2) under the conditions of $\lambda = \lambda'$, T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz; the reflectance as a function of μ_c can be calculated through TMM; and the gate voltage corresponding to the varying μ_c can also be calculated by using Equations (4) and (5). If the initial chemical potential of graphene is 0, that is, the undoped state, then the minimum reflectance point of the SPR curve will occur at the corresponding gate voltage required for the graphene chemical potential to reach the PR point (see Table 1), which may be referred to as the resonance gate voltage. When the initial chemical potential changes from 0 due to the attachment of biomolecules, the minimum reflectance point of the SPR curve is shifted because part of the contribution of the gate voltage applied to bring the chemical potential to the PR point is replaced by the contribution of the attached biomolecules. So, the shift of the gate voltage at the minimum reflectance point (i.e., resonance gate voltage) can be used for indicating the change of the initial chemical potential, and consequently, indicating the attachment of target biomolecules. For the monochromatic incident light with wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, using fixed incident angles of 71.7°, 80.3°, 84.9° , 86.8° , 86.2° and 85.1° , respectively, and adopting the optimal prism materials for different wavelengths, i.e., LF for 1100 nm, CaF₂ for 1200 nm, MgF₂ for 1310, 1550, 1700 and 1900 nm, respectively, the evolution of reflectance versus gate voltage SPR curves with the initial chemical potential change in graphene film are depicted in Figure 11. Here, we assume that both the added gate voltage and the attached biomolecules exert the same doping effect on graphene, i.e., both n-doping or both p-doping. It can be seen that with the increase in the initial chemical potential (absolute value), the resonance gate voltages all shift to smaller values. When using 1100 nm as the incident light wavelength, care should be taken not to make the scanning gate voltage exceed 57.5 V, otherwise the dielectric layer would be broken down, as shown in Figure 11a. We can calculate the CP sensitivities in gate voltage interrogation mode, S'_{CP} , defined as the ratio of the resonance gate voltage change to the initial chemical potential change in the graphene film $\Delta V_{gres}/\Delta CP$. At the

incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm, the values are 156.9822, 143.6147, 131.0779, 111.0351, 101.3415 and 90.6038 mV/meV, respectively. The FWHMs can also be calculated, and the values are 1158, 1394, 1475, 1790, 1522 and 1474 mV, respectively, at the incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The FOM for chemical potential sensing in gate voltage interrogation mode can be calculated to be 135.6, 103.0, 88.9, 62.2, 66.6 and 61.5 eV⁻¹, respectively, at the incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. According to Equation (5), the same change of chemical potential in a higher chemical potential value region leads to a larger change of the charge carrier density (thus leading to a larger change in the gate voltage that is to be applied). As the μ_{cPR} decreases with the increase in wavelength (see Table 1), CP sensitivity (S'_{CP}) decreases with the increase in incident light wavelength, as shown in Figure 12. For the chemical potential shift of >10 meV caused by the hybridization of 0.01 nM complimentary DNAs to the probe DNAs pre-fixed to the graphene [57], the resonance gate voltage would shift > 1569.822, >1436.147, >1310.779, >1110.351, >1013.415 and >906.038 mV, respectively, at the incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. The minimum detection limit of the sensor in biosensing in gate voltage interrogation mode is related to the resolution of DAC. The output voltage of DAC is in fact discrete with a minimum step equal to $\delta V_{DAC} = V_{REF}/(2^{M} - 1)$, where M is the bit number of a DAC and V_{REF} is the reference voltage (full scale output) [35]. Since the maximum gate voltage should not exceed 57.5 V, the reference voltage is set to be V_{REF} = 57 V. For a 24-bit DAC, δV_{DAC} = 3.4 μ V. Suppose the proposed near-infrared GSPR sensor is used in DNA sensing described in Ref. [57]; it can reach surprising theoretical LOD of <21.66, <23.67, <25.94, <30.62, <33.55 and <37.53 aM in gate voltage interrogation mode, respectively, at the incident wavelengths of 1100, 1200, 1310, 1550, 1700 and 1900 nm. If a DAC with a larger bit number M is adopted, it is conceivable that the LOD will decrease further.



Figure 11. The evolution of reflectance versus gate voltage SPR curves at the incident wavelengths of (**a**) 1100; (**b**) 1200; (**c**) 1310; (**d**) 1550; (**e**) 1700; (**f**) 1900 nm with the initial chemical potential change in the graphene film.



Figure 12. CP sensitivities (S'_{cp}) of the sensor in gate voltage interrogation mode at different incident light wavelengths.

4. Discussion on the Influence of the Quality and the Atom Layer Number of the Graphene Film on the Sensing Performance

As a graphene-based SPR sensor, its performance is strongly influenced by the quality and the atom layer number of the graphene film. Compared with other preparation methods such as mechanical exfoliation from bulk graphite and graphitization of silicon carbide substrate, chemical vapor deposition on transition metals exhibits its superiority from the relatively simple and low-cost growth, large size, mass production, and ease of transfer to other substrates. However, due to point defects, surface contaminations, and especially line defects induced by grain boundaries, CVD graphene generally suffers severe degradation of its charge carrier mobility μ (typically with the mean value of approximately $1100 \text{ cm}^2/(\text{V} \cdot \text{s}))$ [61]. Extensive efforts have been devoted to the promotion of the quality of CVD graphene. Solid-diffusion-facilitated cleaning of copper foil allows CVD graphene with lower grain density and larger size of single crystalline domains, and the mobility of up to 5400 $\text{cm}^2/(\text{V}\cdot\text{s})$ is achieved [62]. Employing Cu-Ni alloy foil instead of pure Cu foil offers a promising route for the efficient preparation of CVD graphene showing a typical single-crystalline nature with the absence of grain boundaries [63]. The quality of CVD graphene is not only mainly determined by an as-synthetic process, but also by defects incurred during the transfer process. Employing polyvinyl acetate (PVAc) as a novel support layer during the transfer process enables CVD graphene to achieve a high carrier mobility of up to 10,000 cm²/(V·s) [64]. Furthermore, in biosensing, graphene is inevitably exposed to ionic solution, which can improve the carrier mobility of graphene at room temperature by minimizing the long-range Coulomb scattering originated from the charged impurities in the substrate underneath the graphene through ionic screening effect [65]. It can be therefore confirmed that the charge carrier mobility μ of CVD graphene in biosensing is generally in the range of ~ 1000 to $10,000 \text{ cm}^2/(\text{V} \cdot \text{s})$, or even higher. The scattering rates corresponding to charge carrier mobility of 1000 to $10,000 \text{ cm}^2/(\text{V} \cdot \text{s})$ at $\mu_c = 0.594 \text{ eV}$ are $\Gamma = 7.6 \times 10^{12} \text{ to } 7.6 \times 10^{11} \text{ Hz}$ (calculated using $\mu = (\tau e v_F^2) / \mu_c$ [66], and the free carrier relaxation time $\tau = 1/(2\Gamma)$). The influences of the scattering rate Γ and the atom layer number N of the graphene film on the reflectance versus wavelength SPR curve at a resonance wavelength of 1310 nm (as well as the reflectance versus gate voltage SPR curve at an incident wavelength of 1310 nm) is displayed in Figure 13. With the increase in Γ , N meanwhile keeps at 5, and the R_{min} of the reflectance versus wavelength SPR curve increases rapidly while the FWHM increases rapidly, as shown in Figure 13a. The reflectance versus gate voltage SPR curve also displays the same evolution law with the increase in Γ and constant of N, as shown in Figure 13c. With the decrease in N, Γ meanwhile keeps at 1×10^{12} Hz, and the R_{min} of the reflectance versus wavelength SPR

curve increases gradually while the FWHM decreases gradually, as shown in Figure 13b. The reflectance versus gate voltage SPR curve displays the same evolution law with the decrease in N and constant of Γ , as shown in Figure 13d. Obviously, a smaller Γ and larger N (N \leq 5) is beneficial to sensor's high-quality biosensing performance. Recently, the progress in fabrication of high-quality multilayer CVD graphene [67] further enhances the feasibility and efficiency of preparing and operating the proposed near-infrared tunable GSPR biosensor, thus moving the sensor closer to the practical stage.



Figure 13. (a) Reflectance versus wavelength SPR curves at resonance wavelength of 1310 nm for different scattering rate and N = 5; (b) reflectance versus wavelength SPR curves at resonance wavelength of 1310 nm for different atom layer number and $\Gamma = 1 \times 10^{12}$ Hz; (c) reflectance versus gate voltage SPR curves at incident wavelength of 1310 nm for different scattering rate and N = 5; (d) reflectance versus gate voltage SPR curves at incident wavelength of 1310 nm for different atom layer number and $\Gamma = 1 \times 10^{12}$ Hz.

5. Conclusions

This paper proposes and numerically investigates a Kretschmann coupling configuration tunable near-infrared GSPR biosensor. The study found that when the chemical potential of graphene is at the PR points (usually at or near the ENZ points), plasmon resonance can be excited in graphene by near-infrared incident light due to the satisfaction of the momentum matching condition. The PR points in near-infrared spectrum as well as the gate voltages required for the exciting are obtained through calculation. The sensor can operate in wavelength interrogation mode, where a stable applied gate voltage brings the chemical potential of graphene to the PR point, and the shift of resonance wavelength can be used to indicate the attachment of biomolecules. The sensor can also operate in gate voltage interrogation mode, where a scanning gate voltage is applied, and the shift of resonance gate voltage can be used for indicating the initial chemical potential change due to the attachment of biomolecules. The CP sensitivity, FWHM and FOM of the sensor in two operating modes are obtained through calculation. The chemical potential sensing properties of the sensor give it great application potential in high-sensitivity and high-specificity biosensing. It can be expected through calculation that the proposed nearinfrared GSPR sensor can achieve the theoretical LOD as low as or even lower than that of 2D material-enhanced noble metal-based SPR sensors and do not need the help of the synergistic sensitization of AuNPs which are inevitably employed by the latter as sensitive

enhancement strategy in biosensing. Through calculation, the optimal prism materials and the incident angles working at different resonance wavelengths in wavelength interrogation mode (that is, the optimal prism materials and the incident angles working at different incident wavelengths in gate voltage interrogation mode) are studied. The discussion of the influence of graphene quality and atom layer number on the sensing performance demonstrates the feasibility and efficiency of preparing and operating the proposed sensor. The tunable nature of the sensor also facilitates the use of existing mature instruments in the near-infrared region for SPR biosensing.

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Appendix A

The optimal prism material and resonance angles at different incident wavelengths are calculated through the angular interrogation method for Si₃N₄ layer thickness changing within the range of 50–100 nm. In calculation: $t_{Au} = 10$ nm; the refractive index of aqueous solution, analyte layer, and Si₃N₄ are set to 1.33, 1.33, and 2, respectively; the refractive index of graphene for each incident wavelength λ is calculated through Equations (1) and (2) under the condition of T = 298 K, $\Gamma = 1 \times 10^{12}$ Hz, $\mu_c = \mu_{cPR}(\lambda)$.

Table A1. Optimal prism material and resonance angle at different incident wavelength for Si_3N_4 layer thickness changing within the range of 50–100 nm.

Si	₃ N ₄ Layer Thickness	50 nm	60 nm	70 nm	80 nm	90 nm	100 nm
1100 nm	optimal prism resonance angle	LF 71.7°	LF 73.4°	LF 75.2°	Topaz 75.3°	Topaz 77.2°	Topaz 78.9°
1200 nm	optimal prism resonance angle	CaF ₂ 80.3°	ZBLAN 78.9°	ZBLAN 80.7°	ВК7 79.7°	BK7 81.6°	BK7 83°
1310 nm	optimal prism resonance angle	MgF ₂ 84.9°	CaF ₂ 81.8°	CaF ₂ 83.7°	CaF_2 85°	ZBLAN 84.1°	ZBLAN 85.4°
1550 nm	optimal prism resonance angle	$\begin{array}{c}MgF_{2}\\86.8^{\circ}\end{array}$	MgF ₂ 87.7°	MgF ₂ 87.3°	CaF ₂ 84.9°	CaF ₂ 86.9°	CaF ₂ 87.9°
1700 nm	optimal prism resonance angle	MgF ₂ 86.2°	MgF ₂ 87.9°	$\begin{array}{c} MgF_2 \\ 88.5^{\circ} \end{array}$	MgF ₂ 87.7°	CaF ₂ 85.3°	CaF ₂ 87.3°
1900 nm	optimal prism resonance angle	MgF ₂ 85.1°	MgF ₂ 86.8°	$\frac{MgF_2}{88.5^\circ}$	$\frac{MgF_2}{89^\circ}$	MgF ₂ 88.1°	CaF_2 85°

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