

Band structure and dispersion engineering of strongly coupled plasmon-phonon-polaritons in graphene-integrated structures

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Abstract: We theoretically investigate the polaritonic band structure and dispersion properties of graphene using transfer matrix methods, with strongly coupled graphene plasmons (GPs) and molecular infrared vibrations as a representative example. Two common geometrical configurations are considered: graphene coupled subwavelength dielectric grating (GSWDG) and graphene nanoribbons (GNR). By exploiting the dispersion and the band structure, we show the possibility of tailoring desired polaritonic behavior in each of the two configurations. We compare the strength of coupling occurring in both structures and find that the interaction is stronger in GNR than that of GSWDG structure as a result of the stronger field confinement of the edge modes. The band structure and dispersion analysis not only sheds light on the physics of the hybridized polariton formation but also offers insight into tailoring the optical response of graphene light-matter interactions for numerous applications, such as biomolecular sensing and detection.

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1. Introduction

Light interacts with matter by the exchange of photons [1–6]. If such interaction is strong enough to overcome decoherence effects, matter enters the strong coupling regime, forming new light-matter states or quasi-particles known as polaritons [3–6]. Such states are separated by an energy bandgap (i.e., the Rabi splitting) as a result of the band anticrossing behavior. These polaritonic states exhibit exotic behavior distinct from both light and matter, spurring significant research activity into cavity electrodynamics with applications ranging from polariton diode and lasing [7–9], polariton Bose-Einstein condensation [10, 11], optical amplification [12], to quantum information processing [13]. Clearly, a crucial aspect behind these applications is the control over the light-matter interaction and consequently, the polaritonic dispersion and band structure.

Traditional platforms to achieve strong light-matter interactions center on maximizing the quality factor over the effective mode volume (Q/V), which is proportional to the Purcell factor, through the use of microcavities or structured noble metals [14–26]. Recently, graphene has been recognized as a versatile plasmonic material in mid-infrared to terahertz frequencies [27–34]. The collective oscillation of carrier density in graphene under optical excitation gives rise to the emergence of the plasmon modes which are longer-lived and much more highly confined in compared to the plasmons in noble metals [35–42]. Due to higher- Q and smaller effective mode volume (i.e., higher Purcell factor), as well as the intrinsic planar nature of graphene which ensures its accessibility to external changes in the environment, graphene plasmons (GPs) offer better opportunities to investigate the strong coupling phenomena and explore diverse applications, e.g. biosensing [43–52]. In addition, the Fermi level of graphene can be tuned by electrical gating or chemical doping [28], which provides additional degree of freedom to manipulate the polaritons. It has been shown that graphene plasmons can couple with graphene intrinsic optical phonons [53], phonons in polar substrates (e.g., SiO_2 , SiC, and h-BN) [53–58], and extrinsic vibrational modes of adsorbed molecules [59]. In each of these cases, graphene plasmon-phonon polaritons are formed in the strong coupling regime. To the best of our knowledge, however, a detailed, general theoretical investigation and in-depth understanding on the dispersion and the band structure of polaritons in graphene-integrated structures is still lacking.

In this paper, we analytically investigate the polaritonic dispersion and band structure via the transfer matrix method (TMM) within the framework of classical electrodynamics. This provides for a more intuitive understanding compared to existing approaches e.g. modeling the polariton from two independently driven coupled oscillators (similar to Fano resonances) [60–62], or via solving the quantum mechanical eigenvalue problem of the interaction Hamiltonian [16, 21, 22, 62]. We consider a representative example, the case of coupling between GPs and vibrational modes of external adsorbates on graphene. In particular, two common excitation geometries for GPs are examined: graphene coupled with one-dimensional subwavelength dielectric gratings (1D GSWDGs) and graphene nanoribbons (GNRs). The resultant optical responses are compared and characterized as a function of their respective geometric parameters and graphene doping levels. Finally, we further validate our methods by analysing the strong coupling between GPs and polar substrate phonons. This study not only leads to a better understanding of the strong coupling between light and matter in graphene-integrated structures, but also provides useful guidelines for their design in various potential applications.

The paper is organized as follows. In section 2, we introduce the TMM to analytically solve the graphene plasmon-phonon polariton dispersion. In Section 3, the excitation conditions for polariton resonance and the band structures of GSWDG and GNR structures are introduced. This analysis takes into account the influence of carrier localization in the latter geometry, via effective conductivity and ribbon width corrections. In Subsection 3.1, under normally inci-

dent illumination, we compare the numerically calculated response via finite element method (FEM) of COMSOL with the analytical dispersion via TMM in both structures. Based on the excitation techniques, we further discuss the possibilities of tailoring the desired polaritons via manipulation of the dispersion curve, which is achieved by tuning the geometry or the graphene doping levels. In Subsection 3.2, the polariton band structures for both geometrical configurations are presented. We extend this study to oblique incidence angles, and show that each of the anticrossing polariton bands splits a second time due to the broken symmetry. We further validate our model by analysing the strong coupling to polar substrate in section 4. Finally, we present our discussion and conclusions in section 5.

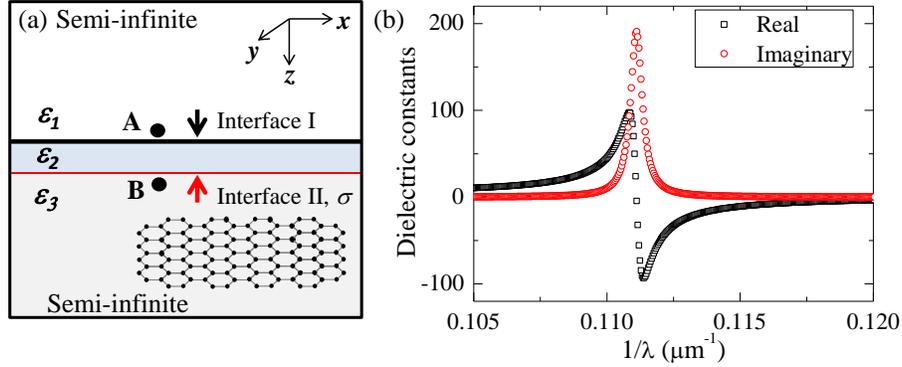


Fig. 1. (a) The schematic diagram of a sandwiched structure which consists of graphene layer at the interface II. The optical conductivity of graphene is denoted as σ . The dielectric constants of the sandwiched structure are ϵ_1 , ϵ_2 , and ϵ_3 , respectively. The electric or magnetic field of point A and that of point B can be related by a transmission matrix. (b) The real and imaginary parts of the dielectric constant ϵ_2 as a function of frequency. The Drude-Lorentz model is applied to simulate the molecular dipoles in medium 2. In the calculations, $\epsilon_\infty = 2$, $\omega_m = 0.111 \mu\text{m}^{-1}$, $\omega_p = 2 \times 10^{14} \text{ rad s}^{-1}$, and $\gamma_m = 1 \times 10^{12} \text{ rad s}^{-1}$.

2. The polaritonic dispersion

To start, consider a sandwiched structure in which medium 2 is separated by semi-infinite media 1 and 3 via interface I and II, respectively [Fig. 1(a)]. A monolayer graphene with optical conductivity σ is introduced at the interface II [Fig. 1(a), inset]. Within the local random-phase approximation [63, 64], the conductivity is modelled as

$$\sigma(\omega) = \frac{2ie^2k_B T}{\pi\hbar^2(\omega + i\tau^{-1})} \ln \left[2 \cosh \left(\frac{E_F}{2k_B T} \right) \right] + \frac{e^2}{4\hbar} \left[\left(\frac{1}{2} + \frac{1}{\pi} \arctan \left(\frac{\hbar\omega - 2E_F}{2k_B T} \right) \right) - \frac{i}{\pi} \ln \left| \frac{\hbar\omega + 2E_F}{\hbar\omega - 2E_F} \right| \right], \quad (1)$$

where ω is the angular frequency, e is the charge of an electron, k_B is the Boltzmann constant, \hbar is the reduced Planck constant, E_F is the Fermi level, τ is the intrinsic relaxation time, and T denotes the temperature in Kelvin. The Drude-like first term in the equation describes the free-carrier response for intraband transitions and the second term is responsible for the interband transitions. When the incident photon energy is lower than $2E_F$, the intraband transition dominates and the graphene exhibits metallic behavior and is capable of supporting plasmon modes. The dielectric constants in the three regions are described by ϵ_1 , ϵ_2 , and ϵ_3 , respectively. Under p -polarized light illumination (i.e., \mathbf{H} field in the y direction) from medium 1, the electromagnetic wave propagates in sequence across interface I, the homogeneous medium 2 with the thickness of d , and the interface II. Utilizing the transmission matrix [65], the magnetic

field at the proximity of interface I (point A in Fig. 1(a)) can be related to that of interface II (point B in Fig.1 (a)) via the following 2×2 matrices:

$$\mathcal{M}_{1 \rightarrow 2} = \frac{1}{2} \begin{pmatrix} 1 + \eta_{21} & 1 - \eta_{21} \\ 1 - \eta_{21} & 1 + \eta_{21} \end{pmatrix}, \quad (2)$$

$$\mathcal{M}_{2 \rightarrow 2}(d) = \begin{pmatrix} e^{-ik_{2z}d} & 0 \\ 0 & e^{ik_{2z}d} \end{pmatrix}, \quad (3)$$

$$\mathcal{M}_{2 \rightarrow 3} = \frac{1}{2} \begin{pmatrix} 1 + \eta_{32} + \xi_{23} & 1 - \eta_{32} - \xi_{23} \\ 1 - \eta_{32} + \xi_{23} & 1 + \eta_{32} - \xi_{23} \end{pmatrix}, \quad (4)$$

where $\mathcal{M}_{i \rightarrow j}$ denotes the transmission matrix of light propagation across the interface from medium i to j , $\mathcal{M}_{i \rightarrow i}(d)$ is the matrix of light transmitting a distance d in the i th medium, $\eta_{ij} = (\epsilon_j k_{iz}) / (\epsilon_i k_{jz})$, $\xi_{ij} = (\sigma k_{jz}) / (\epsilon_0 \epsilon_j \omega)$, k_{iz} is the z component of the wave-vector $k_i = \sqrt{\epsilon_i} \omega / c$ in the i th medium, ϵ_0 is the vacuum permittivity, and c is the speed of light. The incident angle θ is defined as $\arccos(k_{1z}/k_1)$. By assuming the incident amplitude to be unity, the field relation between A and B point as shown in Fig. 1(a) is obtained:

$$\begin{pmatrix} 1 \\ r \end{pmatrix} = \mathcal{M}_{1 \rightarrow 2} \mathcal{M}_{2 \rightarrow 2}(d) \mathcal{M}_{2 \rightarrow 3} \begin{pmatrix} t \\ 0 \end{pmatrix}, \quad (5)$$

where r and t are reflection and transmission coefficients of the structure, respectively. Since the modes of plasmons or polaritons exist merely at the interface, hinting that r has poles, namely,

$$(1 + \eta_{21})(1 + \eta_{32} + \xi_{23})e^{-ik_{2z}d} + (1 - \eta_{21})(1 - \eta_{32} + \xi_{23})e^{ik_{2z}d} = 0. \quad (6)$$

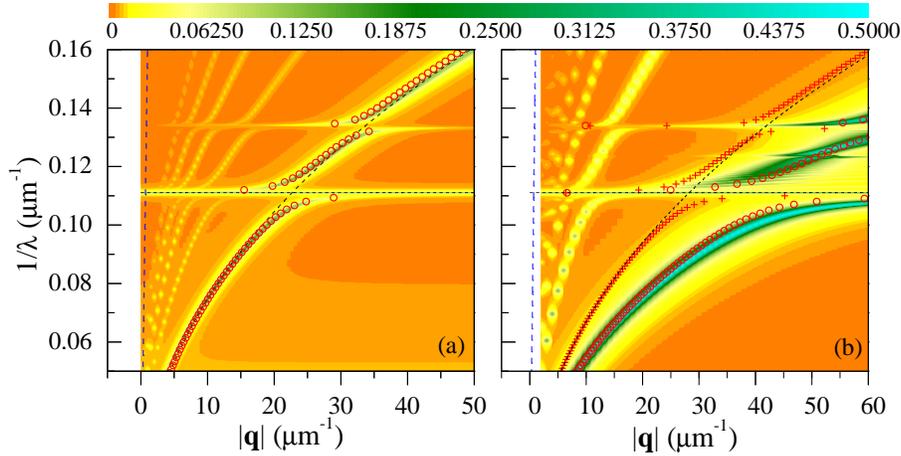


Fig. 2. The analytical dispersion and the numerical absorption spectra (the colored contour) for the polaritons in GSWDG (a) and GNR (b) configuration, respectively. The red open circles in (a) and crosses in (b) are calculated by σ which describes the optical conductivity of a continuous graphene sheet. However, the red open circles in (b) are calculated with the effective conductivity $\sigma_1^{\text{eff}}(\omega)$. The light line is denoted as the blue dashed lines in both panels. For both structures, the band splitting at the molecular resonance are observed, which is ascribed to the anticrossing behavior of GP band and the molecular resonance (black dashed lines). It is clear that the coupling in GNR is much stronger than that in GSWDG structure.

In system with external adsorbates, such as biomolecules, the GPs are capable of coupling to the molecular vibrations (e.g., in medium 2), resulting in graphene plasmon-phonon-polariton modes which are confined at graphene surface [47, 48]. The z components of the wavevector of polaritons are imaginary. Therefore, k_{2z} can be rewritten in the form of ik'_{2z} where k'_{2z} is a real number. After some algebra, we obtain the analytical dispersion for graphene plasmon-phonon-polariton

$$\tanh(k'_{2z}d) = -\frac{1 + \xi_{23} + \eta_{21}\eta_{32}}{(1 + \xi_{23})\eta_{21} + \eta_{32}}. \quad (7)$$

In the non-retarded regime, $|\mathbf{q}| \gg |\mathbf{k}_{1(3)}|$, where $|\mathbf{q}|$ is the magnitude of the in-plane wave vector $|\mathbf{q}|$ (i.e., polariton wave vector). However, for the molecular layer, it reads $|\mathbf{q}| \approx |\mathbf{k}_2|$ due to large values of the dielectric constant near the molecular resonant frequency ω_m as shown in Fig. 1(b). The dielectric constant ϵ_2 of the molecular layer is modelled using Drude-Lorentz type dispersion as

$$\epsilon_2 = \epsilon_\infty + \frac{\omega_p^2}{\omega_m^2 - \omega^2 - i\gamma_m\omega}, \quad (8)$$

where ω_p is the plasmon frequency, γ_m is the damping frequency for molecules, and ϵ_∞ is the dielectric constant of the system at infinite frequencies.

In this paper, we assume the plasmon frequency $\omega_p = 2 \times 10^{14}$ rad s⁻¹, $\gamma_m = 1 \times 10^{12}$ rad s⁻¹, $\omega_m = 0.111 \mu\text{m}^{-1}$ (i.e., $\lambda_m = 9 \mu\text{m}$), $\epsilon_\infty = 2$, $E_F = 0.4$ eV, an intrinsic relaxation time of $\tau = 0.4$ ps, and $T = 300$ K (unless otherwise specified in the following simulations). Subsequently, by applying Eq. (7) together with the parameters $l = 1$ nm, $\epsilon_1 = 1$ (air), $\epsilon_3 = 1.65$ or 2.3, the analytical dispersions of the polariton are calculated in Fig. 2(a) and 2(b) (red open circles and red crosses), respectively. The dispersion curves of GPs and molecular resonance modes are also plotted for comparison (black dashed lines in both panels). We note here the GP dispersion curves are calculated by assuming that medium 2 is filled with a 1-nm-thick dielectric layer with $\epsilon_2 = \epsilon_\infty$. From the figures, it is clearly observed that an anticrossing gap occurs at the molecular resonance. In the vicinity of the molecular resonance, the dispersion curves of the polariton become flat, indicating their molecular origin. However, this dispersion turns to be identical with that of GPs apart from the resonant frequency, manifesting plasmonic feature in nature. In addition, a subsidiary anticrossing gap is observed with its central frequency higher than the molecular one, which is actually the coupling between the high order of the collective molecular modes and the GPs.

3. Polariton excitation and band structure

The intrinsic polariton modes cannot be excited in the geometry discussed above because the dispersion lies well under the light line [blue dashed lines in Fig. 2(a) and 2(b)]. Subsequently, compensating the mismatch of the momentum is necessary for polariton-excitation. The general approaches to introduce \mathbf{G}_x are to incorporate subwavelength dielectric grating structure into graphene [38, 39] or to pattern the graphene into discrete nanoribbon structures [40–42]. The analytical expression for the polariton excitation can be, therefore, expressed as

$$|\mathbf{q}| = |\mathbf{k}_x| + j|\mathbf{G}_x|, \quad (9)$$

where \mathbf{k}_x is the in-plane wave vector of the incident light, \mathbf{G}_x is the induced additional reciprocal vector, and j is an integer.

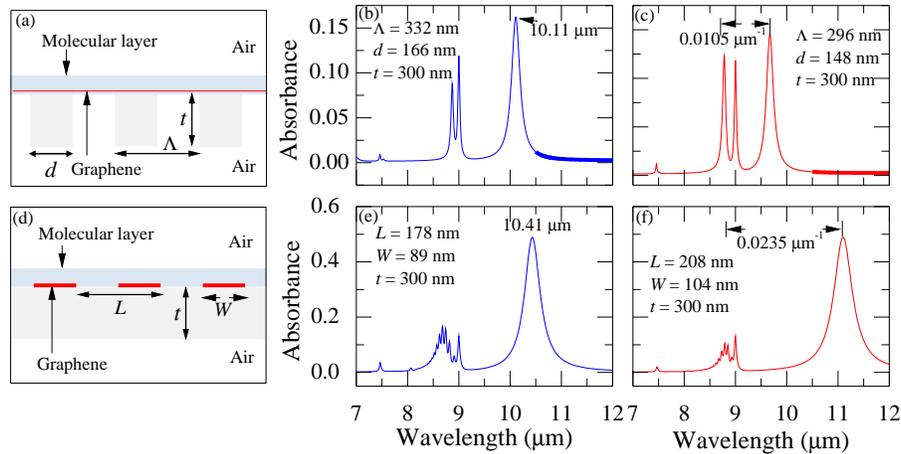


Fig. 3. The polariton excitation configurations [(a) and (d)] and the polaritonic features under normal incidence [(b), (c), (e), and (f)]. The numerically calculated spectra in (b) and (e) show only 1.1% and 4.1% difference from the results tailored by the polariton dispersion in wavelength for GSWDG (a) and GNR (d) structure, respectively. Similarly, the bandgap can also be designed via the dispersion curves. The results show only 0.45% and 3.15% discrepancy for the structures of (a) and (d), respectively.

3.1. Normal incidence

3.1.1. Tailoring the polariton via GSWDG structure

The profile of GSWDG structure is determined by the periodicity of the underlying grating Λ , the grating width D , and the grating thickness t [Fig. 3(a)]. By varying the dielectric material of the structure and its parameters, the polaritonic resonance can be almost arbitrarily engineered. Without loss of generality, we assume the resonance occurs at $10.0 \mu\text{m}$ ($0.10 \mu\text{m}^{-1}$ in frequency). From the dispersion [red open circles in Fig. 2(a)], the in-plane wave vector for the lower polariton branch, is found to be $18.91 \mu\text{m}^{-1}$. With normal incident light ($k_x = 0$) and $j = 1$, the polariton excitation condition turns to

$$|\mathbf{q}| = |\mathbf{G}_x| = 2\pi/\Lambda. \quad (10)$$

Therefore, the periodicity is calculated as 332 nm. Since the wavelength of the incident light is much larger than the dimensions of the grating, effective medium theory is applied to determine the material filling factor f of the grating via the equation $\epsilon_3 = f\epsilon + (1-f)$ [66], where ϵ_3 taken to be 1.65 and ϵ is the dielectric constant of the grating material. Assuming $\epsilon = 2.3$, the value of f turns to be 0.5, i.e., the grating width $D = 166 \text{ nm}$. In the z direction, the electromagnetic field of the coupled polariton decays exponentially and the attenuation length is determined by $1/\sqrt{|\mathbf{q}|^2 - k_i^2}$ (typically, $< 100 \text{ nm}$) from which the smallest value of the grating thickness t can be determined. With 300 nm grating thickness, the field cannot probe the outer region of the dielectric grating; therefore, the assumption that medium 3 is semi-infinite physically holds and the analytical dispersion equation remains valid. Following the above structural parameters, the numerical calculations illustrate that one of the polariton peaks is located at $10.11 \mu\text{m}$ which is only 1.1% different from the expected value [Figure 3(b)]. Additionally, the polariton dispersion curve can also be employed to tune the frequency splitting width $\Delta(1/\lambda)$ between the two hybridized modes which is the measurement of the strong coupling strength. For instance, in order to obtain a splitting width $\Delta(1/\lambda) = 0.01 \mu\text{m}^{-1}$, the in-plane wave vector is calculated

to be $21.2 \mu\text{m}^{-1}$ from the dispersion diagram, corresponding to $\Lambda = 296 \text{ nm}$ and $D = 148 \text{ nm}$. The simulation results shown in Fig. 3(c) show the splitting width is $0.0105 \mu\text{m}^{-1}$ in frequency. This is a discrepancy of only 0.45% deviation from the design value following the definition as $\Delta(1/\lambda)/(1/\lambda_m)$.

We further simulate the polariton dispersion by calculating the absorption spectra of GSWDG structure according to the above excitation techniques [the color-filled contour in Fig. 2(a)]. From the contour, anticrossing behaviors between the molecular resonances and the GPs can be observed explicitly. Several analogous branches of the polariton modes are identified, which result from the interactions between the higher order GPs and the molecular resonance. Compared with the fundamental mode coupling, the analytical dispersion illustrates almost identical features with the numerically simulated absorption.

3.1.2. Tailoring the polariton via GNR structure

Unlike the GSWDG structure, the discrete patterning of the graphene sheet in the GNR structure enables the excitation of localized plasmons which can be hybridized with the adsorbed molecules. These localized plasmons in the ribbon must satisfy the condition $m\lambda_p/2 \sim W$ (i.e., $|\mathbf{q}| = m\pi/W$, where λ_p is the excited polariton wavelength, W is the nanoribbon width, and m is the number of the half wavelength [40–42]). By incorporating the polariton dispersion, the light wavelength which can excite the resonance λ_{res} is determined. However, the above standing-wave resonance condition is not precise due to the induced phase changes at the boundaries of the nanoribbon. The phase changes should be taken into account in the excitation condition. By including the induced phase changes, the condition of polariton resonance can be rewritten as

$$|\mathbf{q}|W + 2\phi_m = m\pi, (m = 1, 2, \dots), \quad (11)$$

where ϕ_m is the phase change of the m -th order resonance at the ends of the GNR. As mentioned before, the polaritons own the plasmonic features in nature, thus the study results from the GPs can be well extended to polaritons in GNR structures, and vice versa.

Recent work on the localized plasmons in GNR structures have shed light on the so-called edge modes, in which the first-order and second-order modes exhibit a dispersion different from that of the bulk modes [41]. The experimental measurements in terahertz regime show the obvious discrepancies up to even 25% from the expected bulk plasmon frequency which follows the relation

$$\omega_p^s = \sqrt{\frac{\sigma(\omega = 0)|\mathbf{q}|}{2\varepsilon_0\varepsilon_{\text{avg}}\tau}}, \quad (12)$$

where ω_p^s is the frequency for the bulk GP mode, ε_{avg} is the average value of the dielectric constant on either side of the GNR, and $\sigma(\omega) = \sigma(\omega = 0)(i/\tau)/(\omega + i/\tau)$. One approach to improve the accuracy is to treat the plasmon current density distribution as a forced vibration problem. The fundamental mode follows [41]

$$\omega_{p0}^s = \alpha \sqrt{\frac{1.156\sigma(\omega = 0)}{\varepsilon_0\varepsilon_{\text{avg}}\tau W}}, \quad (13)$$

where ω_{p0}^s is the plasmon frequency of the fundamental mode and α is a coefficient responsible for the interactions between the neighboring localized plasmons in ribbon structures. The value of α has been found to be ~ 0.95 for a ratio of the nanoribbon width W to the periodicity L around 0.5 [41]. Comparing Eq. (12) with Eq. (13), it follows that $|\mathbf{q}| = 2.087/W$. Substituting the result into Eq. (11), the phase change for the fundamental mode reads $2\phi_1 = 0.3355\pi$. Accordingly, we can define the effective ribbon width \tilde{W}_m , namely

$$|\mathbf{q}|\tilde{W}_m = m\pi, (m = 1, 2, \dots), \quad (14)$$

where $\tilde{W}_1 = 1.505W$ for fundamental mode in an excellent agreement with the experimental fitting data [42, 53]. Hence, under normal light illumination ($|\mathbf{k}_x| = 0$), the polariton excitation condition in GNR for the fundamental mode, reads

$$|\mathbf{q}| = |\mathbf{G}_x| = \pi/(1.505W). \quad (15)$$

Alternatively, one can retain the excitation condition as $m\pi/W$ and the polariton dispersion can be corrected by the introduction of “effective conductivity” of graphene $\sigma_m^{\text{eff}}(\omega)$. From Eq. (11) and the definition of $\sigma(\omega)$, it is easily to obtain the relation of $\sigma_1^{\text{eff}}(\omega) = \sigma(\omega)/1.505$ for the fundamental modes. The analytical polariton dispersion derived from the effective conductivity $\sigma_1^{\text{eff}}(\omega)$ is given in Fig. 2(b) (red open circles). It is observed that the dispersion curve calculated by the effective conductivity is shifted downwards together with a wider anticrossing bandgap, indicative of stronger confinement compared to the modes in GSWDG structure.

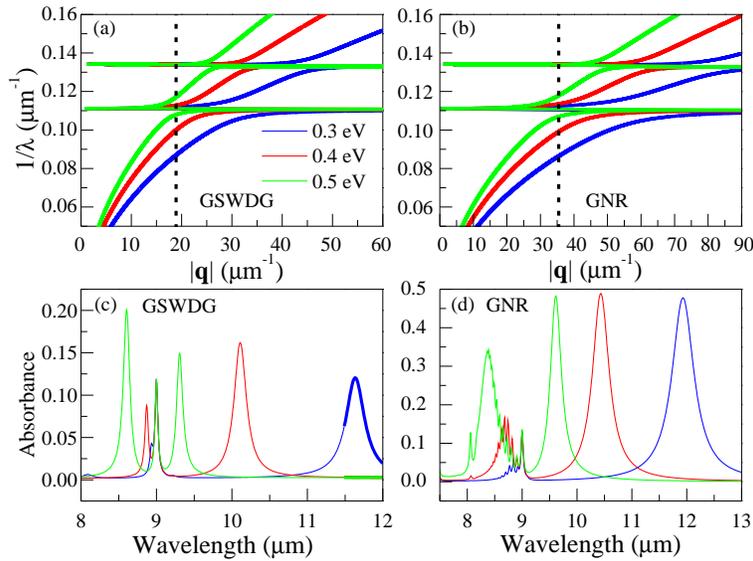


Fig. 4. The analytical polariton dispersion dependence on graphene doping levels for the GSWDG (a) and GNR (b) structures are simulated, respectively. The numerically calculated results for the GSWDG (c) and GNR (d) structures show excellent agreements with that of analytical results. In the calculations, $\Lambda = 332$ nm, $d = 166$ nm for GSWDG structure; $L = 178$ nm, $W = 89$ nm for GNR structure.

With the above knowledge in mind, now we can engineer the polariton spectra on demand in GNR structure [Fig. 3(d)]. Similarly, with the desired operating frequency at $0.10 \mu\text{m}^{-1}$, the in-plane wave vector, e.g., for the lower polariton branch, reads $23.55 \mu\text{m}^{-1}$ [from the red cross curve] which corresponds to an effective ribbon width of 133 nm. That is, the ribbon width W is determined to be 89 nm, which can also be obtained directly from the $\sigma_1^{\text{eff}}(\omega)$ -derived dispersion curve (where $|\mathbf{q}|$ reads $35.44 \mu\text{m}^{-1}$ [from the red circle curve]). The simulated spectra [Fig. 3(e)] show an absorption peak located at $10.41 \mu\text{m}$, a 4.1% deviation from the analytical value. A fixed frequency splitting width, e.g., $\Delta(1/\lambda) = 0.02 \mu\text{m}^{-1}$ (the minimum band splitting is $\sim 0.012 \mu\text{m}^{-1}$), determines that the wave vector $|\mathbf{q}|$ is $30.10 \mu\text{m}^{-1}$ from the $\sigma_1^{\text{eff}}(\omega)$ -derived dispersion, resulting in $W = L/2 = 104$ nm. Figure 3(f) show the simulated polariton spectra according to the predetermined geometry, in which a band splitting of $0.0235 \mu\text{m}^{-1}$ is obtained. This is again only a 3.15% difference from the analytically determined design values. In our

calculations, the substrate thickness t is assumed to be 300 nm, the same as for the GSWDG structures.

By simulating the absorption spectra under normal illumination at different periodicity, the polaritonic dispersion in the ribbon structures is readily obtained [color-filled contour in Fig. 2(b)]. As expected, anticrossing behavior is observed at the molecular infrared resonance, in good agreement with the analytical derivation. The numerical results illustrate as well the several analogous branches as a result of higher order polaritonic resonances sustained by the ribbons. Compared with the GSWDG structures, the GNR structures show much stronger infrared absorption as well as larger Rabi splitting bandgap, which are signatures of stronger coupling between the GPs and the vibrational phonons as a result of stronger GP localization. Further inspection of the simulated polariton dispersion in GNR structures reveal that several flat bands emerge in higher frequency side of the main anticrossing gap, which manifest themselves as small oscillations imposed on the peak of the shorter wavelength in the absorption spectra, as shown in Fig. 3(e) and 3(f). The imposed oscillations can be ascribed to the resonant cavities formed by the neighboring ribbons.

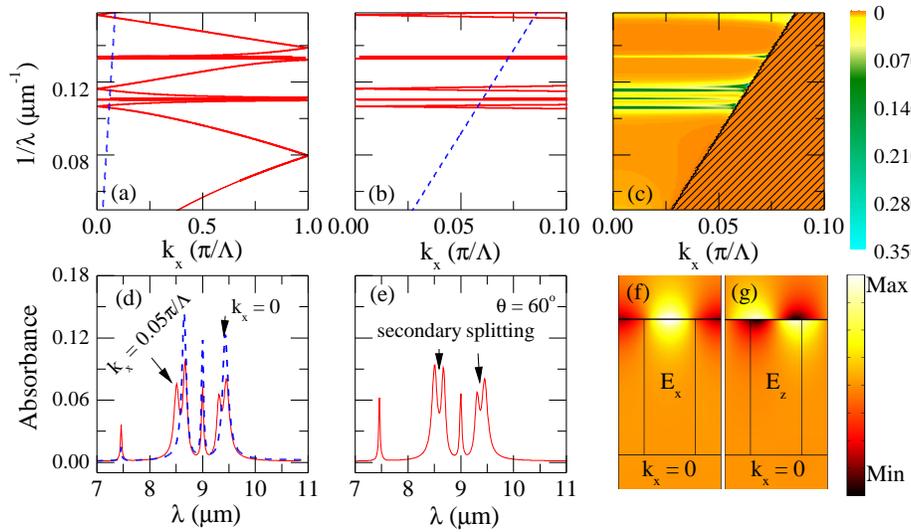


Fig. 5. (a) The polaritonic band structure (red solid line) and the light line (blue dashed line). (b) The enlarged plot of the band structure in (a) above the light line (blue dashed line). (c) The calculated absorbance as a function of in-plane wave vector and frequency. Excellent agreements between the analytical and numerical results are clearly observed. (d) The absorbance under $\mathbf{k}_x = 0.05\pi/\Lambda$ (red solid line) and $\mathbf{k}_x = 0$ (blue dashed line). (e) The absorbance under the incident angle $\theta = 60^\circ$. Both (d) and (e) show the secondary band splitting which is ascribed to the broken symmetry. (f) and (g) Distribution of electric field intensity at the wavelength $8.66 \mu\text{m}$ in the x and z direction, respectively. All the results are obtained with the structure of GSWDG coupled to the molecular layer. The parameters of the structure are $\Lambda = 272 \text{ nm}$, $D = 136 \text{ nm}$, $t = 0.3 \mu\text{m}$, $d = 1 \text{ nm}$, $\epsilon = 2.3$, and $E_F = 0.4 \text{ eV}$.

3.1.3. Tailoring the polariton via graphene doping

Unlike noble metals, the Fermi level of graphene itself can be tuned dynamically by electrical gating or chemical doping [28], which offers us an additional freedom to manipulate the graphene plasmon-phonon polariton dispersion. Figure 4(a) and 4(b) illustrate the analytical dispersion curves with different graphene doping levels (e.g., 0.3 or 0.5 eV), while all other

parameters remaining unchanged compared with that of $E_F = 0.4$ eV in previous calculations [red curves in Fig. 4 for comparison], in GSWDG and GNR configurations, respectively. σ_1^{eff} is adopted to calculate the dispersion curve of GNR structure. It is clearly observed that the dispersion is “pushed” downwards as E_F decreases, indicating stronger polariton confinement, in analogous with that of graphene plasmon behaving. By assuming $|\mathbf{q}| = 18.91 \mu\text{m}^{-1}$ [black dashed line in Fig. 4(a)], the excitation wavelengths of the lower polariton branch for GSWDG structure shift to $0.087 \mu\text{m}^{-1}$ ($11.50 \mu\text{m}$) for $E_F = 0.3$ eV or $0.108 \mu\text{m}^{-1}$ ($9.26 \mu\text{m}$) for $E_F = 0.5$ eV from $0.1 \mu\text{m}^{-1}$ ($10.0 \mu\text{m}$) for $E_F = 0.4$ eV. In addition, the splitting width changes to $0.0264 \mu\text{m}^{-1}$ or $0.009 \mu\text{m}^{-1}$ for $E_F = 0.3$ eV or 0.5 eV, respectively. Similarly, by setting $|\mathbf{q}| = 35.44 \mu\text{m}^{-1}$ [black dashed line in Fig. 4(b)], the excited lower polariton mode is determined to be $0.086 \mu\text{m}^{-1}$ ($11.6 \mu\text{m}$) or $0.107 \mu\text{m}^{-1}$ ($9.35 \mu\text{m}$) and the splitting width is $0.0266 \mu\text{m}^{-1}$ or $0.009 \mu\text{m}^{-1}$ for $E_F = 0.3$ eV and 0.5 eV, respectively. All results show excellent agreement with the numerical calculations [Fig. 4(c) and 4(d)].

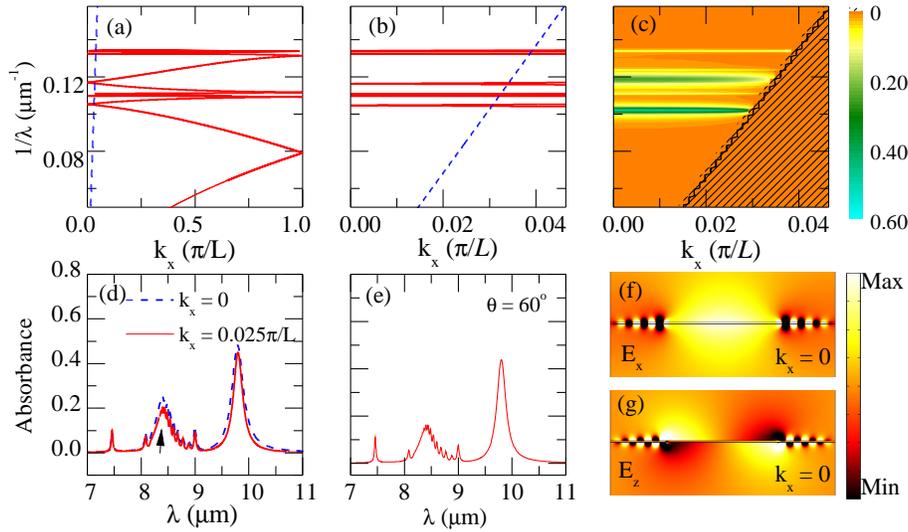


Fig. 6. (Similar with Fig. 5 but with the structure of GNR coupled with the molecular layer. The introduction of $\sigma_1^{\text{eff}}(\omega)$ deduced from the fundamental plasmon modes gives rise to the polaritonic band structures in (a) and (b). Compared with Fig. 5, the band structure and the absorption spectra (c) show larger band splitting, flatter bands, and stronger absorption. Flat bands further render the insignificant secondary band splitting under oblique incidence, as shown in (d) and (e). This is ascribed by the stronger interaction between the edge mode supported by the GNR structure and the molecular dipoles. From (f) and (g) with the wavelength $8.4 \mu\text{m}$ of the incident light (marked by the black solid arrow in (d)), polaritonic standing waves occur between the neighboring ribbons, which explains the origin of the small oscillations imposed on the main absorption peak. The parameters of the structure are $L = 146$ nm, $W = 73$ nm, $t = 0.3 \mu\text{m}$, $d = 1$ nm, $\varepsilon = 2.3$, and $E_F = 0.4$ eV.

3.2. Polariton band structure and secondary band splitting under oblique incidence

To investigate the case that $\mathbf{k}_x \neq 0$ (i.e., oblique incidence), the polariton band structures are calculated for both the GSWDG and GNR structures.

3.2.1. GSWDG structure

For a fixed GSWDG structure (e.g., $D = 136$ nm and $\Lambda = 272$ nm), the analytical polariton band structure [Fig. 5(a)] is readily obtained by folding the analytical dispersion curve shown in Fig. 2(a) at the reduced first Brillouin zone edge (i.e., $\pi/\Lambda = 11.55 \mu\text{m}^{-1}$). Flat bands and bandgaps are observed in the enlarged diagram of the band structure above the light line [Fig. 5(b)]. In Particular, a band emerges at the resonance of the molecular dipoles. From the band structures, it is observed that the polariton mode splits for a second time, due to the symmetry breaking under $\mathbf{k}_x \neq 0$. As a comparison, the absorbance spectra of the structure as a function of in-plane wave vector and frequency, which illustrates the band structure numerically, are calculated [Fig. 5(c)]. The overall correspondence is clearly observed between the analytical and numerical results. Figure 5(d) and 5(e) show the absorption spectra with $\mathbf{k}_x = 0.05\pi/\Lambda$ and $\theta = 60^\circ$, respectively (red solid lines). As expected, the secondary band splitting gives rise to the emergence of more absorption peaks compared with that of normal incidence [blue dashed line in Fig. 5(d)]. Finally, Figure 5(f) and 5(g) show the x and z component of the electric field of the excited polariton at $8.66 \mu\text{m}$ respectively, which show similar field distribution like the edge mode of localized GPs [40].

3.2.2. GNR structure

Similarly, we repeat the calculation for the GNR structure. The analytical band structure, the enlarged band structure above the light line, and the numerical absorbance spectra are depicted in Fig. 6(a), 6(b), and 6(c) respectively. In the calculations, the ribbon width W is assumed to be 73 nm and $L = 146$ nm in order to spectrally match the molecular dipole resonance. Because σ is not well-defined in the GNR structure, here we only plot the band structure calculated by σ_1^{eff} which accurately illustrates the band splitting between the fundamental GP and the molecular resonance. Obviously, compared with the GSWDG structure, the band splitting is larger and the intensity of the resonances is stronger. Importantly, the bands are much flatter, leading to negligible secondary band splitting even under large \mathbf{k}_x , e.g., $0.025\pi/L$ [red solid line in Fig. 6(d); The blue dashed line is for $\mathbf{k}_x = 0.$] or large incident angle, e.g., 60° [Fig. 6(e)]. From Fig. 6(d) and 6(e), it is also observed explicitly that small oscillations are imposed on the main absorption peak of the polariton at shorter wavelengths. This is induced by the standing waves of the polariton formed between the neighboring nanoribbons which are clearly shown in the electric field distribution in the x and z direction at the wavelength marked by the arrow in Fig. 6(d) [Fig. 6(f) and 6(g)], respectively.

4. Extended validation

To further validate our model and method in engineering the graphene plasmon-phonon polaritons, we use the structure of GNR coupled with polar substrate as another example [Fig. 7(a)]. Physically, such configuration can be related to the configuration shown in Fig. 1(a) if we now treat medium 2 as polar substrate and assume the light is propagating from medium 3 to 1. As a result, the field relation between B and A point can be obtained:

$$\begin{pmatrix} 1 \\ r \end{pmatrix} = \mathcal{M}_{3 \rightarrow 2} \mathcal{M}_{2 \rightarrow 2}(d) \mathcal{M}_{2 \rightarrow 1} \begin{pmatrix} t \\ 0 \end{pmatrix}, \quad (16)$$

According the same procedures shown in the previous section, the analytical dispersion for such polariton is deduced as

$$\tanh(k'_{2z}d) = -\frac{1 + \eta_{12}(\eta_{23} + \xi_{32})}{\eta_{12} + \eta_{23} + \xi_{32}}. \quad (17)$$

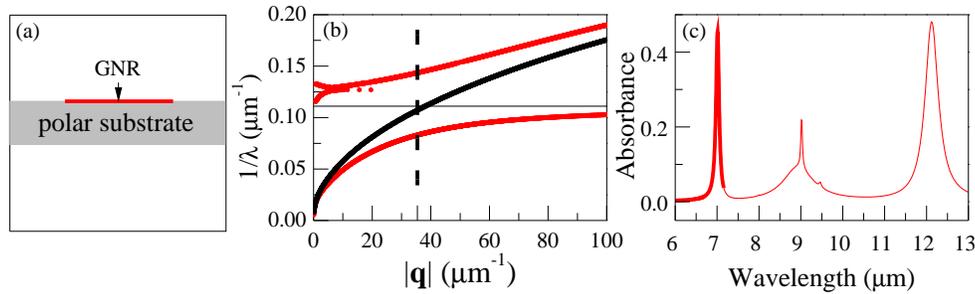


Fig. 7. (a) The configuration of GNR structure coupled with polar substrate in one unit cell. (b) The analytical polariton dispersion from Eq. (17) (red solid circles). The GP dispersion and the substrate phonon mode are identified by the solid black lines. (c) The numerical results show excellent agreement with the prediction results by setting $|q| = 35.44 \mu\text{m}^{-1}$ (dashed line in panel (b)). In the calculations, $L = 178 \text{ nm}$, $W = 89 \text{ nm}$ for GNR structure, and $l = 300 \text{ nm}$ for the polar substrate.

For simplicity and without loss of generality, all parameters used to model the polar substrate are the same with that of molecules in that the Drude-Lorentz dispersion as they are still valid for polar crystal [67]. Assuming the thickness of the polar substrate $l = 300 \text{ nm}$, the typical oxide layer thickness such as SiO_2/Si used in Ref. [53], and $\epsilon_1 = \epsilon_3 = 1$, Figure 7(b) plots the analytical dispersions of such polariton (solid red circles). The dispersion curves of the GPs and the substrate phonons are also plotted for comparison (solid black). Again by assuming $|q| = 35.44 \mu\text{m}^{-1}$ [dashed line in Fig. 7(b)], the polariton modes are predicted at $0.0829 \mu\text{m}^{-1}$ ($12.06 \mu\text{m}$) and $0.145 \mu\text{m}^{-1}$ ($6.90 \mu\text{m}$), which are in excellent agreement with the numerical calculations [Fig. 7(c)].

5. Discussion and conclusions

Strong light-matter coupling is studied extensively in microcavities or nanoplasmonic structures where the photonic or plasmonic resonances can interact with optically active materials (e.g., semiconductors) to form the hybridized polaritons. As mentioned in the introduction, the traditional approaches to obtain the polaritonic bands are via coupled classical oscillator approach within the framework of classical mechanics or by solving the eigenvalue problem of the interaction Hamiltonian within quantum mechanics. Here we successfully begin with Maxwells equations and extend the TMM to solve the problem of light-matter interaction, with the coupling of GPs and molecular vibrational phonons as a representative case. The method intuitively illustrates how the electromagnetic field propagates inside the hybrid system and better helps the understanding on how the polariton anticrossing band emerges. With this method, it is possible to obtain the analytical dispersion and band structure of the graphene plasmon-phonon-polariton that is in good accordance with that from rigorous fully vectorial numerical solvers of Maxwell equations. By utilizing both the dispersion curve and band structure, the graphene-plasmon-phonon strong coupling can be designed and tailored according to the “fingerprint” infrared absorption of different molecular dipoles, with for e.g. significant implications for targeted sensing and identification of biomolecules. Importantly, for a fixed geometry, we note that the polariton dispersion and band structure can be further manipulated by the tuning of E_F which offers one more degree of freedom.

Looking at graphene polariton formation in greater detail, it is seen that while the GSWDG structure already serves as a very sensitive platform for strong coupling between light and matter due to the intrinsic carrier properties of graphene, the GNR configuration is found to be

an even superior platform for the hybridized mode formation. These results can be understood by considering the stronger near-field confinement from the plasmon localization: the edge modes sustained in GR structure can exchange energy with the molecular infrared vibration modes with higher efficiency.

The GSWDG structure can render a periodic modulation of graphene conductivity via extrinsic doping, which would further modify the band structure [68]. This effect is not considered in our study, because of the impact of the modulated periodic graphene conductivity on the band structure from dielectric gratings is substantially weaker than the contribution from the grating periodicity itself. However, for GNR, the modification of the graphene conductivity due to the accumulated carriers at either ends of the ribbon play a key role in the plasmon excitation, leading to tremendous deviation in optical response compared to prediction from the conductivity of pristine graphene. The previous experimental work usually introduces a fitting width of the ribbon which is called as the effective width in order to make up the discrepancy. However, due to lack of well-defined conductivity, the uneven carrier distribution makes it still a challenging task to obtain the band structure of GNR. In our studies, we introduce the effective conductivities $\sigma_m^{\text{eff}}(\omega)$ from which the analytical band structure is figured out. Alternatively, we can parametrize the equations in terms of the effective width \tilde{W}_m of the GNR, which is in good agreement with the experimental fitting values [42, 53].

With illumination at normal incidence, the high and low frequency branches of the polariton dispersion originate from the anticrossing behavior, known as Rabi splitting, of the GP band and the molecular dipole resonance. Under oblique angles, each mode splits for a second time, giving rise to the so-called secondary band splitting. The effect of this band splitting is weaker in GNR compared with the GSWDG, which can be understood by the stronger field confinement and flatter band dispersion induced by the localization of the polaritons in the GNR structure. To inhibit the secondary band splitting in the GSWDG, Fabry-Pérot resonant cavity can be coupled into the above systems [47], in which destructive interference can be employed to eliminate the undesired polariton by adjusting the cavity dimension.

In conclusion, using strongly coupled GPs and the vibrational phonons of molecular dipoles in both the GSWDG and GNR configurations as a representative example, we extend TMM, particularly with the aid of $\sigma_m^{\text{eff}}(\omega)$ or \tilde{W}_m in GNR, to investigate the polariton dispersion and band structure. The analytical results are in good agreement with that from the numerical calculations. With the analytical dispersion and band structure, we show the possibility on tailoring desired polaritonic behavior in each of the two configurations. We further reveal that the interaction between the GPs and the vibrational phonons is stronger in GNR than that of GSWDG structure as a result of stronger field confinement. The dispersion and band structure studied in the paper not only helps the understanding of the graphene plasmon-phonon-polariton hybridization but also provides an insightful method and a good opportunity on the novel application exploration in graphene-integrated nanophotonics.

Acknowledgment

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