Novel mid-infrared plasmonic properties of bilayer graphene

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We study the mid-infrared plasmonic response in Bernal-stacked bilayer graphene. Unlike its monolayer counterpart, bilayer graphene accommodates optically active phonon modes and a resonant interband transition at infrared frequencies. They strongly modifies the properties of bilayer graphene, leading to Fano-type resonances, giant plasmonic enhancement of infrared phonon absorption, narrow window of optical transparency, and a new plasmonic mode at higher energy than the classical plasmon.

Plasmonics1 is an important subfield of photonics that deals with the excitation, manipulation, and utilization of plasmons-polaritons.2 It is a key element of nanophotonics,3 metamaterials with novel electromagnetic phenomena4,5 and also has potential applications in biosensing6. Recently, graphene has emerged as a promising platform for plasmonics7. It has many desirable properties such as gate-tunability, extreme light confinement, long plasmon lifetime, and plasmonic resonances in the terahertz to mid-infrared (IR) regime.8,9 Spatially resolved propagating plasmons has been observed with scanning near-field optical microscope10,11. Tunable plasmon resonances in the terahertz12 to IR13 has been observed in graphene micro- and nano-ribbons, and the relative damping pathways have also been studied.14 Identified applications for graphene plasmonics range from notch filters15, polarizers and modulators16,17 to beam reflectarrays18. Identified applications for graphene plasmonics range from notch filters15, polarizers and modulators16,17 to beam reflectarrays18, biosensing19 and IR photodetectors20 via bolometric effect22.

In this paper, we discuss why Bernal AB-stacked bilayer graphene is important and interesting in its own right as a plasmonic material. Apart from a few theoretical studies of plasmons in bilayer graphene23–25, there is still no experimental studies of bilayer graphene plasmonics. First indication that the plasmonic response in bilayer graphene might be very different than that of monolayer is its two prominent IR structures in its optical conductivity. IR optical measurements of bilayer graphene reveal a phonon peak at $\omega \approx 0.2$ eV, with a strong dependence of peak intensity and Fano-type line-shape on the applied gate voltage.29–30. This interband coupling in bilayer graphene also results in two nested bands, which presents a set of doping dependent IR features31,32. This interband transitions between the two nested bands produced a conductivity peak at $\omega \approx 0.4$ eV in optical IR measurements.34–36. The impact of these IR structures on the bilayer plasmonic response has not been studied. We found several novel plasmonic effects in bilayer graphene: (i) giant plasmonic enhancement of infrared phonon absorption, (ii) an extremely narrow optical transparency window, and (iii) a new plasmonic mode at higher energy than the classical plasmon.

Bilayer graphene arranged in the Bernal AB stacking order is considered, with basis atoms $A_1$, $B_1$ and $A_2$, $B_2$ in the top and bottom layers respectively. The intralayer coupling is $\gamma_0 \approx 3$ eV and the interlayer coupling between $A_2$ and $B_1$ is $\gamma_1 \approx 0.39$ eV, an average of values reported in optical IR and photomission measurements.34–38. We work within the $4 \times 4$ atomic $p_z$ orbitals basis, i.e. $a^\dagger_{1k\parallel}, b^\dagger_{1k\parallel}, a^\dagger_{2k\parallel}, b^\dagger_{2k\parallel}$, where $a^\dagger_{1k\parallel}$ and $b^\dagger_{1k\parallel}$ are creation operators for the $i$th layer on the $A/B$ sublattices. Within this basis, the Hamiltonian near the $K$ point can be written as: $\mathcal{H}_k = v_f \mathbf{p} \cdot \mathbf{E}_s + $ \begin{align*}
&\pm \frac{1}{\sqrt{2}} \sigma_z \otimes \sigma_s + \frac{\alpha}{\sqrt{8}} \sigma_x \otimes \sigma_s + \frac{\Delta}{\sqrt{16}} \sigma_y \otimes \sigma_s + \frac{1}{\sqrt{2}} \sigma_y \otimes \sigma_s, \end{align*}
where $\sigma_i$ and $I$ are the Pauli and identity matrices respectively. We defined $\sigma_{\pm} = \frac{1}{2}(\sigma_z \pm i\sigma_y)$ and $\Delta$ is the electrostatic potential difference between the two layers. Expressions for non-interacting ground state electronic bands $\xi_n(k) \ (n = 1, 4)$, see inset of Fig.1 and wavefunctions $\Phi_n(k)$ are obtained by diagonalizing $\mathcal{H}_k$, see Suppl. Info.

We consider coupling of long wavelength longitudinal/transverse optical (LO/TO) phonons near $\Gamma$ point with the graphene plasmons. Relative displacement of the two sublattices in the top layer ($T$) is given by,

$$u_T(r) = \sqrt{\frac{\hbar}{2 \rho_m \omega_{op}}} \sum_{p\Lambda} \langle \hat{b}_p + \hat{b}_p^{\dagger} \rangle e^{i p \cdot r}$$

where $\mathcal{A}$ is the area of the unit cell, $\rho_m$ is the mass density of graphene, $p = (p_x, p_y)$ is the phonon wavevector, $\lambda$ denotes the LO/TO modes where $\hat{b}_p^{\dagger}$ is its creation operators, $e_{\Lambda}(p)$ are the polarization vectors given by $e_{\text{LO}}(p) = i (\cos \varphi, \sin \varphi)$ and $e_{\text{TO}}(p) = i (-\sin \varphi, \cos \varphi)$ where $\varphi = \tan^{-1}(p_y/p_x)$. Due to the two graphene layers, there are two possible vibrational modes i.e. symmetric ($u_B(r) = u_T(r)$) and antisymmetric ($u_B(r) = -u_T(r)$), where subscript $B$ denotes bottom layer. Hence, the electron-phonon coupling at the $K$ valley for bilayer
The plasmonic response of bilayer graphene can be obtained from its dielectric function given by,

$$\epsilon_{\tau}^{p}(q, \omega) = \kappa - v_c \Pi^0_{\rho,\rho}(q, \omega) - v_c \frac{q^2}{\omega^2} \delta \Pi_{j,j}(q, \omega),$$  \hspace{1cm} (5)

at arbitrary wave-vector $q$ and frequency $\omega$. $v_c = e^2/2q\varepsilon_0$ is the 2D Coulomb interaction and $\kappa$ is the effective dielectric constant of the environment. $\Pi^0_{\rho,\rho}(q, \omega)$ is the non-interacting part (i.e. the pair bubble diagram) of the charge-charge correlation function given by[40, 41],

$$\Pi^0_{\rho,\rho}(q, \omega) = -\frac{g_\sigma g_v}{(2\pi)^2} \sum_{m,n} \int dk \times$$

$$\frac{n_F(\xi_n(k)) - n_F(\xi_n'(k + q))}{\xi_n(k) - \xi_n'(k + q) + \hbar \omega + i\hbar/\tau_e} |F_{n,n'}(k, q)|^2$$  \hspace{1cm} (6)

where $n_F$ is the Fermi-Dirac distribution function, $g_\sigma$ and $g_v$ are the spin/valley degeneracy, $F_{n,n'}(k, q) = \Phi_n(k) |\Phi_{n'}(k + q)|$ is the band overlap, and $\tau_e$ is the electron lifetime, where we assumed a typical experimental value of $\eta \equiv \hbar/\tau_e \approx 10 \text{meV}$[18].

The effect of electron-phonon interaction is included within $\delta \Pi_{j,j}(q, \omega)$, where subscript $j$ denotes the current operator. Here, we employ a model for $\delta \Pi_{j,j}(q, \omega)$ which is consistent with the various electron-phonon selection rules for the symmetric/antisymmetric modes and Fano effect observed in optical spectroscopy experiments for bilayer graphene. The detailed implementation follows a formalism known as the charged-phonon theory[42, 43],

$$\delta \Pi_{j,j}(q, \omega) = \sum_{\nu\nu'} \Gamma_{j,\nu}(q, \omega) D_{\nu\nu'}(\omega) \Gamma_{\nu'j}(q, \omega)$$  \hspace{1cm} (7)

where

$$\Gamma_{j,\nu}(q, \omega) = \frac{e^2\omega}{\hbar} \Pi^0_{\rho,\rho}(q, \omega) + \frac{e^2\omega}{\hbar} \delta \Pi_{j,j}(q, \omega)$$  \hspace{1cm} (8)

FIG. 1: Real part of bulk bilayer graphene conductivity (solid line) computed at $T = 300 \text{K}$ at chemical potential of $\mu = 0.3 \text{eV}$, constant damping of $\eta = 10 \text{meV}$, zero gap (i.e. $\Delta = 0 \text{eV}$) and $q = 0$. This is compared with the case where $\gamma_1 = 0 \text{eV}$ (dashed line). $\sigma_0$ is universal conductivity of $e^2/2h$.
FIG. 2: (a) shows the RPA electron loss function $L(q, \omega)$ for bilayer graphene computed at $T = 300$ K at chemical potential of $\mu = 0.3$ eV, constant damping of $\eta = 10$ meV, zero energy gap (i.e. $\Delta = 0$ eV) and a background dielectric constant of $\kappa = 2.5$. Green lines are boundaries for the Landau damped regions. Spectra at different plasmon momenta $q$ are plotted in (b).

This mode is responsible for the sharp resonance feature at $\omega = \omega_{\text{op}}$.

Longitudinal collective plasmonic dispersion is obtained by looking for the zeros in the real part of the dynamical dielectric function i.e. $\text{Re}[\epsilon_T^{\text{rpa}}(q, \omega)] = 0$. For bilayer graphene, there are three solutions: (1) intraband, (2) electron-hole interband and (3) low-energy interband. The $\sqrt{q}$-plasmon lies above the intraband continuum, and compares well with the long wavelength dispersion $\omega_{\text{pl}}(q)$, while the $\gamma$-plasmon is significantly broadened. The most important result is the appearance of a distinctive sharp structure near $\omega \approx \omega_{\text{op}}$, not seen in monolayer graphene.

Our observation in the IR activity of the phonon mode as the plasmon resonance approaches $\omega_{\text{op}}$. The transfer of plasmonic spectral weight to the IR phonon mode, as reflected by an increase in both intensity and linewidth, enhances with decreasing detuning. Renormalized by many-body interactions, this 'dressed' phonon exhibits pronounced IR activity, and is also accompanied by a Fano asymmetric spectral line-shapes. The Fano feature is acquired through interference between the discrete phonon mode and the 'leaky' plasmonic mode; the electronic lifetime is significantly shorter than that of the phonon, broadening the former into a quasi-continuum. The loss spectra show the evolution of the plasmonic and phonon resonances as they approach each other. They evolve from separate resonances at small $q$ to a Fano line-shape, and eventually an induced narrow transparency at zero detuning. This very narrow transparent window emerged within the broadly opaque plasmonic absorption, a phenomenon analogous to the electromagnetically-induced transparency and should also be accompanied by novel electromagnetic effects such as slow light. On the contrary, plasmon coupling with substrate surface optical phonons typically leads to well-separated resonances instead.

Transmission spectroscopy studies has proven to be very effective in probing the plasmonic properties of graphene, where finite plasmon momentum $q$ can be sampled by simply patterning graphene into nanostructures. Graphene nanostructures with dimensions down to 100 nm would allow us to access these predicted mid-IR plasmonic features under experimentally accessible doping conditions. The enhancement of IR phonon activity with decreased detuning between the phonon and plasmon resonance might lead to interesting applications. Indeed, such plasmon-enhanced IR absorption has permitted an emerging field...
of spectroscopy by noble metals of surfaces and electrochemical systems. Tunable plasmonic resonance in graphene nanostructured surfaces might allow for detection of molecules through enhancement of its IR vibrational modes.

Previously, we have seen that the $\gamma$-plasmon mode is overdamped. In the limit of small momenta, it has the following dispersion:

$$\omega_{\gamma}(q) = \frac{1}{\hbar} \left[ \gamma + \frac{q^2}{8\pi \epsilon_0} \log \left( 1 + \frac{2\mu}{\gamma} \right) \right]. \quad (12)$$

If the $\gamma$-plasmon gains sufficient oscillator strength, e.g. by modifying its doping ($\gamma\mu$) or dielectric environment ($\gamma\kappa$), it can reside outside the low-energy interband continuum. This is shown in Fig. 3 (dashed line), calculated using Eq. 12 assuming $\mu = 0.6$ eV and $\kappa = 1$. The electron loss function in Fig. 3 indicates several interesting features of this high energy $\gamma$-plasmon mode. First, its dispersion departs from the simple $\omega_{\gamma} = \gamma \propto q$ relation, acquiring an increasingly $q^2$ behavior with $q$. We find that the modified dispersion can be described within a model that accounts for the effective coupling between the classical and $\gamma$-plasmon as follows,

$$\epsilon_{\text{eff}} \approx \kappa \left[ 1 - \frac{\omega_{\text{pl}}^2}{\omega^2} - \frac{\alpha^2}{\omega^2 - \omega_0^2 + \alpha^2} \right]. \quad (13)$$

where $\alpha$ is an effective coupling between the two modes. Using the long-wavelength expressions for these modes, i.e. Eq. 11 and 12 (dashed white lines), and a coupling energy $\alpha = 85$ meV, the coupled mode solutions (solid white lines) obtained by solving for $\epsilon_{\text{eff}} = 0$ agrees well with the dispersions observed in the loss function. Second, we observed prominent spectral weight transfer from the conventional 2D plasmon to the $\gamma$-plasmon mode. Fig. 3 plots the calculated $L(q, \omega)$ and $L(q, \omega)/\omega$ spectra at typical values of $q = 2 - 10 \times 10^7$ m$^{-1}$. The integrated loss function $\int_L(q, \omega) d\omega$ is related to the Coulomb energy stored in the electron fluid. On the other hand, through the Kramers-Kronig relations, one can obtain the sum rule $\int_0^\infty L(q, \omega)/\omega d\omega = -1/\pi \frac{\Delta}{\omega_0}$, with conserved spectral weight at different $q$. We see that the $\gamma$-plasmon acquires a spectral weight an order larger than the conventional plasmon as the latter enters into the Landau damped region. Hence, it should be experimentally observable. The possibility of an ‘optical’-like high energy plasmonic mode, previously presumed to be overdamped with little spectral weight, might open up applications in higher mid-IR spectral range. With high enough doping, e.g. with electrolyte gating, this mode can gain enough oscillator strength and be pushed out of the Landau damped region, to become a coherent plasmonic mode.

In summary, we have shown that bilayer graphene as a new plasmonic material, is important and interesting in its own right. The above-mentioned new mid-IR plasmonic effects can also be generalized to more complex graphene stacks, for example ABC or ABA trilayers. These new plasmonic resonant features can also potentially lead to interesting applications such as engineered metamaterials with novel electromagnetic effects, resonant heat transfer processes, among many others.

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FIG. 3: (a) shows the RPA electron loss function $L(q, \omega)$ for bilayer graphene computed at $T = 300$ K at chemical potential of $\mu = 0.6$ eV, constant damping of $\eta = 10$ meV, zero energy gap (i.e. $\Delta = 0$ eV) and a background dielectric constant of $\kappa = 1$. Spectra $L$ (solid lines) and $L/\omega$ (dashed lines) at different plasmon momenta $q$ are plotted in (b).

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