Surface Plasmon Engineering in Graphene Functionalized with Organic Molecules: A Multiscale Theoretical Investigation

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ABSTRACT: Graphene was recently shown to support deep subwavelength surface plasmons at terahertz frequencies characterized by low energy loss and strong field localization, both highly desirable. The properties of graphene can be locally tuned by applying an external gate voltage or by the adsorption of organic molecules that lead to doping through charge transfer. Local tuning of the electronic features of graphene opens the possibility to realize any desired gradient index profile and thus brings large flexibility to control and manipulate the propagation of surface plasmons. Here, we explore this possibility created by functionalizing graphene with organic molecules. We employ a multiscale theoretical approach that combines first-principles electronic structure calculations and finite-difference time-domain simulations coupled by surface conductivity. We show that by patterning two types of organic molecules on graphene, a plasmonic metasurface can be realized with any gradient effective refractive index profile to manipulate surface plasmon beams as desired. The special properties of such devices based on functionalized graphene are compared to the similar metamaterials based on metallic films on top of a gradient index dielectric substrate. Using this idea, we design and analyze an ultrathin broadband THz plasmonic lens as proof-of-concept, while more sophisticated index profiles can also be realized and various plasmonic applications are readily accessible.

KEYWORDS: Surface plasmon, metamaterials, graphene, functionalization, DFT, FDTD

Tailoring electromagnetic response at the micro and nanoscales has been a long sought goal that could be reached by artificially structured materials known as metamaterials. Recent advances in metamaterials have enabled a wide range of applications including high-gain nanoantennas, invisibility cloaking, light focusing and collimating, and beam steering. These functions can be realized by manipulation of the electromagnetic field through gradient refractive index (GRIN) in space. To reduce the size and improve the performance of optoelectronic devices, surface plasmons (SP) at the interface of a metal and a dielectric are typically used to manipulate light at the subwavelength scale through collective electron oscillations. The GRIN has been recently extended to manipulate SPs. Because the SP field penetrates into both the metal and the dielectric on either side of the interface, the indices of both materials affect the SP properties. The index of the dielectric can be changed by mixing two materials together with different weights or by drilling air holes of different sizes. By tuning the dielectric part alone, metamaterials for plasmonic applications such as cloaking, concentrators, and beam shifters have been produced. Spatial tuning of the metallic side properties has proven more difficult. Here, we explore a new class of ultrathin plasmonic metasurfaces with any designed GRIN profile based on patterned graphene with organic molecules.

Graphene, a two-dimensional sheet of carbon atoms arranged in a honeycomb lattice, has been observed to support deep subwavelength SPs with highly desirable properties of low energy loss and strong field localization. Tunability is one of the most desirable properties for graphene-based applications. Gate bias provides temporal tunability while patterning molecules enables spatial tunability. Several applications employing gate bias considered so far include modulators, switches, and reconfigurable terahertz antennas, but this approach is severely limited when accurate and complex spatial tunability is required. Specifically, if we assume that each discrete element needs to be controlled on the two-dimensional (2D) surface, the path of the gate bias would become complicated, and the field propagation may be affected by the spatially distributed gates. For these reasons, row-by-row control is typically adopted in the local gate bias, and point-by-point control is avoided. In a recent report, however, a design with connected elements is introduced, in which dc bias at one place is used to control all of the elements. Alternatively, the optical properties of graphene can be tuned through interactions with organic molecules. A variety of
molecules have been shown experimentally to produce n-type or p-type doping in graphene by charge transfer. Using standard patterning processes such as e-beam and dip-pen lithography, it is possible to adsorb molecules on graphene in desired patterns to produce point-by-point spatially tailored features. Figure 1 shows a schematic configuration of the proposed patterned graphene, using two types of molecules, that makes it possible to achieve any desired gradient index profile for the manipulation of SP beams like collimation, bending, focusing and so on. In this work, we investigate the possibility of creating such functionalized graphene metasurfaces using multiscale simulations. We first calculate the optical properties of the graphene–organic molecule complex from first-principles electronic structure methods based on density functional theory (DFT). The calculated surface conductivity is used as input to finite-difference time-domain (FDTD) simulations at the continuum mesoscopic scale to study the SP performance of functionalized graphene. We show that by locally tuning the graphene property point-by-point through molecular patterning, any GRIN profile can be easily achieved. The corresponding SP waves supported by this structure have dispersion properties that are different from traditional plasmonic Selfoc lens, and FDTD simulation result confirms its capability of engineering SP propagation.

Our first-principles calculations are carried out using the SIESTA code25,26 with the LDA exchange-correlation functional. We use a local-basis set of double-ζ polarized atomic orbitals with an energy cutoff of 70 Ry. The structural relaxations are considered converged when the magnitude of the force on each atom was smaller than 0.01 eV/Å.

All of graphene’s atoms are on the same plane that also constitutes its surface. This makes it very susceptible to environment changes such as adsorption of organic molecules.21–24 Organic molecules can induce doping in graphene through charge transfer, which shifts the Fermi level and modifies the joint density of states (JDOS) of the system. As shown in Figure 1, two types of organic molecules, TCNQ+TTF and F4-TCNQ, shift the Fermi level of graphene to 0.16 and 0.4 eV respectively with modified PDOS. These changes also affect optical properties by introducing new optical transitions that depend on the coupling strength, directionality and polarization.

Optical transitions in graphene–organic molecule complex are usually characterized by surface conductivity including both interband and intraband contributions. The contribution of interband transitions is computed directly from the electronic structure of the graphene–organic molecule complex with the coupling and occupation of each pair of states involved in a direct transition calculated and summed over all frequencies.27 The intraband contribution to the surface conductivity is accounted for with the Drude model

\[
\sigma_{\text{intra}}(\omega) = \frac{i \alpha^2 \omega}{(\omega + i\tau)^2}
\]

where the relaxation time \(\tau\) is estimated to be 1 ps based on the experimental data28 and the plasma frequency \(\omega_p\) is computed within DFT using29

\[
\omega_p^2 = \frac{8e^2}{3\Omega} \sum_{k,n} \left| \frac{1}{\hbar} \frac{\partial E_{k,n}}{\partial k} \right|^2 \delta(E_{k,n} - E_F)
\]

where \(k\) is the wave vector, \(e\) is the charge of an electron, and \(\Omega\) is the system volume. \(E_F\) and \(E_{k,n}\) are the Fermi energy and the energy of a state with the summation running over all values of \(k\) and the band index \(n\). Our calculations show that the additional organic molecule states are mostly nondispersive because of the relatively weak interactions with graphene and with each other. Accordingly, the linear dispersion of the graphene Dirac cone is retained but there is local hybridization of the graphene states and the organic molecule states (see Figure S3 in Supporting Information). Equation 2 shows that the plasma frequency is affected by the dispersion close to the Fermi level, which in turn could be sensitive to the graphene–organic molecule interactions.

Before obtaining the conductivity of molecular doped graphene, the conductivity of purely doped graphene with the ideal band structure is developed to test the technical accuracy of the first-principles DFT calculation. The conductivity is

Figure 1. Schematic representation of the graphene structure patterned by organic molecules. The two types of organic molecules used here are TCNQ+TTF (blue area) and F4-TCNQ (green area). The corresponding projected density of states (PDOS) of functionalized graphene areas are plotted with the Fermi level indicated by the dashed vertical line at the zero of the energy scale. The PDOS shows both the effects of doping and the added molecular DOS signature to the total DOS due to the molecule-graphene interactions.
compared to the analytical Kubo formula\textsuperscript{30,31} and good agreement can be seen in Figure S1 of Supporting Information.

Next, the conductivities of graphene doped by F4-TCNQ and TCNQ\textsuperscript{+}TTF are calculated in Figure 2a. In order to show the effect of molecule–graphene interaction, the conductivities of purely doped graphene with the same Fermi levels (0.4 and 0.16 eV) and relaxation time of 1 ps are shown as a comparison.

As mentioned previously, organic molecules do not only induce charge transfer to shift the Fermi level, but also introduce new optical transitions to modify the transport properties. Thus the conductivity differs from that of the pure graphene doped to the same Fermi level and with the same relaxation time. Specifically, the plasma frequency leads to smaller conductivity for both real and imaginary parts at the low frequency range (around below 10 THz). At higher frequencies, the real part of $\sigma_g$ goes above the value for the purely doped case, indicating higher loss for wave propagation. It could be explained by the additional molecular DOS close to the Fermi level in Figure 1. For purely doped graphene, interband transitions impact the optical response only when the frequency satisfies $\hbar\omega > \mu_0^{1/2}$.\textsuperscript{16} For molecular-doped graphene, however, the interband contribution cannot be neglected even at very low frequencies due to the additional transitions involving the molecular states. The ratio between the real part and imaginary part of $\sigma_g$ shows that the loss for molecular doped graphene is comparable to that for purely doped graphene at low frequency range, and it increases slightly at higher frequencies due to the interaction between graphene and molecules. To avoid high loss, we confine the analysis of SP properties to 5–10 THz. (See Figure S5 of Supporting Information for the loss analysis.)

We next study the SP properties in functionalized graphene and how they may be manipulated. We consider a layer of uniformly doped graphene by one type of molecules inserted into the dielectric–dielectric interface. The dispersion relation of SPs at the interface can be calculated from\textsuperscript{14}

$$\omega \varepsilon_{1r} \varepsilon_{2r} \sigma_g \varepsilon_{1r} \varepsilon_{2r} = -\frac{i \sigma_g}{\omega \varepsilon_0} = \frac{\varepsilon_{1r}}{\sqrt{k_y^2 - \omega^2 \mu_0 \mu_0 \varepsilon_{1r} \varepsilon_{1r}}} + \frac{\varepsilon_{2r}}{\sqrt{k_y^2 - \omega^2 \mu_0 \mu_0 \varepsilon_{2r} \varepsilon_0}} \quad (3)$$

This expression is derived from Maxwell’s equations and proper boundary conditions where the conductivity of graphene $\sigma_g$ is obtained from DFT calculations in Figure 2a. $\varepsilon_{1r}$ and $\varepsilon_{2r}$ are the dielectric constants of the materials above and under the graphene layer, and the free-standing case is considered here for simplicity. $k_y$ is the surface wave vector, and the propagation direction is taken along $y$ with the graphene layer in the $y$–$z$ plane throughout this paper. In the nonretarded region ($k_y \gg \omega (\mu_0 \varepsilon_0)^{1/2}$), the dispersion relation can be simplified as

$$k_y = \frac{i \omega \varepsilon_0 (\varepsilon_{1r} + \varepsilon_{2r})}{\sigma_g} \quad (4)$$

The dispersion relations of SPs are shown in Figure 2b for an infinite graphene sheet with uniform adsorption of F4-TCNQ and TCNQ\textsuperscript{+}TTF molecules, respectively. Clearly, the plasmonic properties in graphene could be changed significantly depending on the species of adsorbed organic molecules.
The dispersion curves for traditional SPs supported on gold—dielectric interface with the same wave vectors are also shown in Figure 2b as a comparison and will be analyzed in detail later.

The effective refractive index for the SPs can be extracted from the dispersion relation as $n_{\text{eff}} = c k / \omega$, which indicates the relative scale of the plasmonic wavelength and the free space wavelength. It is of desire to design a metamaterial with gradually changed effective refractive index profile. However, it is unlikely that molecules with different properties can be used to produce a doping profile in graphene with smooth gradient. It is also not practical from the fabrication point of view to mix various molecules with gradient concentrations. Alternatively, we can implement plasmonic GRIN materials using patterned unit cells made of two different types of organic molecules, yielding an effectively smooth GRIN.32

The unit cell of graphene metamaterial, as shown in Figure 1, consists of two patches, one with lower Fermi energy in which TCNQ+-TTF molecules are adsorbed (blue region), and one with higher Fermi energy in which F4-TCNQ molecules are adsorbed (green region). The unit cell size is much smaller than the free space wavelength, and still smaller than one-third of the plasmonic wavelength. Therefore, it can be viewed as homogeneous to a good approximation within a unit cell. SPs are supported by an array of such unit cells with effective refractive index profile $N_{\text{eff}}(yz)$. To clarify, $n_{\text{eff}}$ is used to characterize uniform cells and $N_{\text{eff}}$ is for patterned cells.

We next analyze how $N_{\text{eff}}(yz)$ is modified by the patterns of unit cells with different molecules. For this purpose, we will use the EMT,13 commonly used to describe the effective refractive index of bulk waves in dielectric lattices. First, the homogeneous graphene patch with adsorption of one type of molecules is considered and the refractive indices are calculated as $n_{\text{eff},-2} = c k_{-2}/\omega$ based on the dispersion relation of eq 4 for $n_{\text{eff},-2}$ values that correspond to the (TCNQ+-TTF)-doped and (F4-TCNQ)-doped cases. The SPs act as the bulk wave propagating in a medium with refractive index equivalent to $n_{\text{eff},-2}$. Next, we consider subwavelength unit cells consisting of patches of two such regions. The effective refractive index of the unit cell is determined by the weighting average and can be written as

$$N_{\text{eff}} = (1 - FF^2)n_{\text{eff},-1} + FF^2n_{\text{eff},-2}$$

where FF = $a/b$ is the filling factor as shown in Figure 1. $N_{\text{eff}}$ is shown in Figure 3 as a function of frequency for different FF values. Combinations of the two regions with different weights lead to different $N_{\text{eff}}$ values varying within a large range. By choosing proper FF value for each unit cell, any 2D index profile $N_{\text{eff}}(yz)$ can be easily achieved.

We also carry out full-wave FDTD simulations to confirm the effective refractive index values obtained using periodically patterned unit cells, as a check of the results obtained from EMT. In the FDTD simulation, the atomic layer of graphene is replace by an ultrathin layer of slab with thickness $\Delta = 6$ nm.15

Figure 3. Comparison of calculated effective refractive indices (real part) of metamaterials made of (a) patterned graphene by molecules, and (b) a gold film on top of GRIN dielectric substrate. FF in (b) refers to the relative size of air holes in SiO2 substrate. For both (a,b), the dots are results from full-wave FDTD simulation and the lines are calculated from EMT with FF ranging from 0.0 to 1.0. The arrow in (a) shows the case studied in the Figure S4 of Supporting Information to explain how it is obtained in FDTD.
simplifies to $k_y = (\omega/c)(\varepsilon_d)^{1/2}$. The effective refractive index $N_{\text{eff}}$ of the patterned unit cell is almost a constant in the long wavelength range, as shown in Figure 3b for different filling factors. In contrast to this behavior, the dispersion of 2D electron oscillations in graphene is characterized by a quadratic relation $\omega \propto (k_y)^{1/2}$ at the long wavelength limit, and $N_{\text{eff}}$ is proportional to frequency $N_{\text{eff}} \propto \omega$. The tailored unit cells with different filling factors follow the linear trend shown in Figure 3a. Comparison of Figure 3a,b shows that $N_{\text{eff}}$ is highly dispersive for a patterned-graphene-based unit cell, while it is nondispersive for a gold–dielectric-based metamaterial in the long wavelength limit. This difference originates from the features of 2D and 3D plasmonics mentioned above.

Second, due to the high conductivity of graphene the effective refractive index values in the patterned graphene can be 1 order of magnitude larger than the corresponding values of the gold–dielectric structure. The large effective refractive index requires ultrasmall unit cell size in order to behave as a locally homogeneous medium, which means that the unit cell size may be hundreds of nanometers although it operates in terahertz regime, enabling deep subwavelength structure. Meanwhile, the unit cell size is still well within the reach of current patterning methods like e-beam lithography.

Third, the values of $N_{\text{eff}}$ for the gold–dielectric structure are bounded by the refractive index of the dielectric material, while they can go far beyond the refractive index of the dielectric part for the patterned graphene. Because graphene has all its atoms exposed on its surface, it is extremely sensitive to the adsorption of molecules. The effective refractive index for FF = 0 is almost twice that of FF = 1. This provides a large tuning range since effective indices for other FF values will fall within this range.

Based in Figure 3a, any index profile $N_{\text{eff}}(y,z)$ can be readily achievable by choosing proper filling factors for two types of organic molecules patterned in each unit cell. Taking advantage of the versatile tunability of patterned graphene, we next design a Sloc lens as a proof-of-concept for plasmonic GRIN applications with a quadratic index profile. Sloc lenses are important elements for wave focusing and collimating and can also be used for spatial Fourier transform if the input signal and the probed signal are right at the focal planes before and after the lens.35 To implement a plasmonic version of the Sloc lens, the effective refractive index is uniform in $y$-direction and varies in $z$-direction as

$$N_{\text{eff}}(z) = N_{\text{eff}}(0) \sqrt{1 - \left(\frac{z}{R}\right)^2}$$  \hspace{1cm} (6)

The index profile along the $z$-direction is specified by the smooth dash line in Figure 4 (lower right panel), and the surface wave is propagating in the $y$-direction. $N_{\text{eff}}(0)$ is the effective refractive index at the center in $z$-direction and $R$ is the radius of curvature of the index profile. We use one full-wave FDTD simulation for the whole structure with a point source as the excitation at the frequency of 7 THz. The discretized index profile is indicated by the red solid line in Figure 4 (lower right panel).
panel) with the FFs specified for each unit cell. There are 17 unit cells totally along z-direction, and 13 unit cells along y-direction with a period of 300 nm, as shown in Figure 4 (lower left panel). In the FDTD simulation, the $17 \times 13$ array is patterned exactly with two types of graphene, blue part and green part, with different conductivities resulting from adsorption of two types of molecules. FDTD grids with enough resolution in $x$, $y$, and $z$-directions are chosen to accurately simulate the whole structure. Because of the different phase velocities along the z-axis, the circular surface wave generated from the point source and bound to the surface gradually changes phase front and becomes a surface plane wave at the end of the lens, which is at a distance around 3.9 $\mu$m ($\pi R/2$) from the point source.

The lens functions by design at the frequency 7 THz, but we also checked its broadband performance. In Figure 4 (top set of panels), the performance of the lens is plotted for frequencies from 6 to 8 THz. The collimating effects in this range are as good as at 7 THz with the same focal distance. It is interesting that despite the highly dispersive property of the effective refractive indices for the unit cell, the lens still works in a broadband range. For the functionalized graphene structure, the unit cell is a nonresonant one, but $N_{\text{eff}}$ is linearly increasing with frequency. Because of this linearity, $(N_{\text{eff}}(f_2))/(N_{\text{eff}}(f_1)) = f_1/f_2 = (N_{\text{eff}}(0f_2))/(N_{\text{eff}}(0f_1))$. Thus $N_{\text{eff}}(z)$ and $N_{\text{eff}}(0)$ in eq 6 are scaled by the same factor $f_1/f_2$ and the radius of curvature $R$ of the profile remains the same when the frequency is changed, accommodating a broadband manipulation of the SPs with the same focal distance. From the aspect of EMT, the limit on bandwidth will be as follow. As the frequency increases from the designed 7 THz, the wavelength in free space is decreasing and $N_{\text{eff}}$ is increasing, leading to the decrease of plasmonic wavelength with a higher speed. Hence there is an upper limit for the frequency where the EMT stops working if the plasmonic wavelength is reduced to a value comparable to the unit cell size. As the frequency decreases from 7 THz, we could expect that the plasmonic wavelength is increasing quickly, becoming even larger than the unit cell. The EMT works in a better condition. Obviously, one should be careful about the high loss due to Drude model contribution at very low frequency and high loss due to the molecular contribution at high frequencies.

In addition to the collimating application in Figure 4, the lens can surely be used for focusing and magnifying plasmonic waves when the propagation is in the opposite direction with plane wave excitation. Actually, it is an easy and common way to enhance the resolution and break the diffraction limit by choosing high refractive index materials for the lens. Function-ized graphene supports plasmonic waves with strongly shortened wavelength due to the large $N_{\text{eff}}$ which scales the diffraction limit to the order of $\lambda/2N_{\text{eff}}$. The entire designed lens is 2D atomically thin and its lateral size is only 0.12$\lambda_0$ where $\lambda_0$ is the free space wavelength at 7 THz, while most of the reported lenses$^{35,37}$ have the dimensions comparable to wavelength or even larger. However, it is not easy to be used for imaging since the focusing and magnification effect is not in 3D space but confined on the surface. Nonetheless, such compact atomic-layer device size and the frequency regime make it an attractive approach for sensing applications in biology and pharmacology.

With the development of fabrication technology, the growth and transfer of large-area graphene sheet by chemical vapor deposition (CVD) are becoming mature and standardized processes.$^{38,39}$ The resolution of molecular patterning is well within the reach of e-beam lithography or dip-pen lithography either directly on graphene, or on the substrate, and putting the graphene layer on top of the patterned molecules later. These fabrication techniques enable the potential for experimental verification and practical implementation of functionalized graphene proposed in this paper. It is also worthy to note that it is not essential in practice to form a defect-free closely packed sample as we used in our model for carrying out the calculation.

To summarize, we carried out a multiscale theoretical investigation to study functionalized graphene by organic molecules. The correlation between the electronic structure and the optical properties is analyzed and the device applications are explored. In general, this theoretical tool can be extended into other type of chemical dopants and even other 2D materials beyond graphene to explore new features of atomic layers and devices.

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