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# Using Bottom-Up Lithography and Optical Nonlocality to Create Short-Wave Infrared Plasmonic Resonances in Graphene

Joel. F. Siegel,<sup>#</sup> Jonathan H. Dwyer,<sup>#</sup> Anjali Suresh, Nathaniel S. Safron, Margaret A. Fortman, Chenghao Wan, Jonathan W. Choi, Wei Wei, Vivek Saraswat, Wyatt Behn, Mikhail A. Kats, Michael S. Arnold, Padma Gopalan, and Victor W. Brar<sup>\*</sup>



created using a novel, bottom-up block copolymer lithography method. Measurements of these structures reveal that their plasmonic resonances are strongly influenced by nonlocal and quantum effects, which push their resonant frequency well into the SWIR (free-space wavelength ~2.2  $\mu$ m), 75% higher frequency than previous experimental works. The confinement factors of these resonators reach 137 ± 25, among the largest reported in literature for any type of 2D optical resonator. The combined SWIR response and large confinement of these structures make them an attractive platform to explore ultrastrongly enhanced spontaneous emission.

KEYWORDS: 2D plasmonics, nonlocal effects, bottom-up lithography, tunable plasmonics

ptoelectronic devices based on tunable graphene plasmonic resonances offer a promising route toward next-generation devices<sup>1-3</sup> that include chemical sensors,<sup>4-6</sup> perfect absorbers,<sup>7,8</sup> photodetectors,<sup>9-12</sup> tunable filters,<sup>13</sup> and high-speed intensity and phase modulators.<sup>14,15</sup> Many of these devices require the patterning of graphene sheets into nanoribbons,<sup>5-7,14,16,17</sup> nanoperforated sheets,<sup>4,18,19</sup> or nanodisks<sup>13,18</sup> that support plasmonic oscillations with a resonant frequency set by the characteristic length of the nanostructure and the carrier density of the graphene.<sup>16,18,19</sup> Thus far, these devices have operated at mid- and far-infrared wavelengths. There have been both theoretical<sup>20</sup> and experimental<sup>21,22</sup> investigations that have indicated the plasmonic response of graphene should be heavily damped at free-space wavelengths shorter than 6  $\mu$ m due to plasmon-phonon interactions. Nevertheless, graphene plasmonic resonances at wavelengths as short as 3.5  $\mu$ m have been experimentally observed<sup>16</sup> and, at present, it is not clear if there is a high frequency cutoff for graphene plasmons and, if so, what sets that limit. If the resonant plasmonic response of graphene could be pushed to shorter wavelengths and into the short-wave infrared (SWIR), there would be substantial fundamental and technological implications. For example, theoretical models predict, and experiments demonstrate, that graphene plasmons could create

extremely high Purcell-enhanced rates of emission<sup>16,23,24</sup> and could even be used to drive optically forbidden transitions.<sup>25</sup> These processes are expected to become more dramatic in the SWIR and, unlike the mid-infrared, there are numerous fluorescent SWIR emitters—including quantum dots,<sup>26,27</sup> lanthanide ions,<sup>28</sup> and III–V materials<sup>29</sup>—that can be used as a platform to observe these effects. Meanwhile, from a technological perspective, a tunable SWIR plasmonic response would allow for the creation of high-speed, low-cost devices that operate at telecommunication wavelengths.

To date, however, no experiments have demonstrated a resonant plasmonic response in graphene in the SWIR, largely due to the unique plasmonic dispersion relation in graphene, which leads to a very large mismatch between the plasmonic  $(\lambda_p)$  and free-space wavelengths  $(\lambda_0)$ .<sup>3</sup> For the mid-infrared (MIR), this mismatch, or confinement factor  $(\lambda_0/\lambda_p)$ , is

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**Figure 1.** (a) Overview of the block copolymer (BCP) procedure for fabricating graphene nanoribbons (GNRs), illustrating (top) the sample after BCP deposition, (middle) during RIE etch, and (bottom) after BCP removal. (b) Schematic of experimental device with gold finger contacts and an ionic gel gate placed atop the GNR "zen-garden" (shown as an embedded SEM image). The circuit illustrates the electrical setup where a gate voltage ( $V_G$ ) is applied between the separated areas of graphene and the resistance across the graphene is measured by applying a source/drain bias ( $V_{SD}$ ) across the active area. Insets in (b) illustrate the exaggerated charge density distribution of graphene plasmonic resonances for local and nonlocal, for widths of ribbons 10 and 20 nm.

typically around 50-100. Therefore, to achieve a plasmonic resonance at  $\lambda_0 = 5 \ \mu m$ , graphene nanostructures with 30 nm length scales are needed (the nanostructure width approximately defines  $\lambda_p/2$ ).<sup>16</sup> In the SWIR, however, the confinement factor has been predicted to increase to 100-200,<sup>20</sup> such that achieving resonance at  $\lambda_0 = 2 \ \mu m$  would require patterning the graphene to feature sizes of 8 nm. Creating periodic patterns with these length scales over large (>100  $\mu$ m<sup>2</sup>) areas is difficult for top-down lithography methods such as electronbeam lithography (EBL)-which was previously used to create plasmonic resonators down to 15 nm<sup>16</sup>—due to proximityeffect distortions. Thus, to explore the SWIR regime, new lithographic methods must be developed that are capable of creating graphene nanostructures at sub-15 nm length scales over centimeter-scale areas. A promising alternative to EBL is block copolymer (BCP) lithography, a bottom-up method that creates etch masks with dense nanoscale features over waferscale areas. BCP lithography has been shown to be effective at patterning graphene into nanostructures, including graphene nanoribbons  $(GNR)^{30,31}$  and nanoperforated graphene (NPG).<sup>4,32,3</sup>

In this paper, we show that graphene nanostructures fabricated using BCP lithography down to 12 nm length scales can act as resonant plasmonic cavities with tunable resonant free-space wavelengths down to 2.2  $\mu$ m, substantially shorter than the previous record of 3.5  $\mu$ m.<sup>16</sup> Additionally, the

confinement factors of our devices reach approximately 137, matching the highest experimentally demonstrated value of an optical cavity in a 2D material.<sup>16,34</sup> Our ability to create resonators well into the SWIR is aided by a larger-than-expected blue-shift in the measured resonant frequency of our smallest resonators in comparison to what is predicted by a local electrodynamic model. We attribute this blue-shift to both nonlocal and electron-quantization effects in the GNRs,<sup>35–37</sup> which alter the characteristic scaling laws of plasmonic resonances in sub-15 nm graphene structures.

## RESULTS

**Graphene Nanostructure Fabrication.** We fabricated resonant graphene plasmonic devices using a BCP lithographic process outlined in Figure 1a, where a self-assembled pattern in a BCP film acts as an etch mask for creating graphene nanostructures. Graphene's surface, however, is not energetically favorable for thin film assembly, making it incompatible with standard BCP techniques (see SI, section S1). Two previous approaches to overcoming this challenge involve preassembling the BCP film on a sacrificial substrate and then transferring the preassembled film onto graphene<sup>38</sup>, or depositing BCP on a wetting layer of a thin oxide<sup>32</sup> or poly(dopamine)<sup>39</sup> layer on the graphene. While functional, these methods lead to either significant film loss during the transfer process or an oxide layer on the graphene that can



Figure 2. (a) Schematic of graphene nanoribbons (GNRs) and SEM images containing GNRs with  $29 \pm 3$ ,  $15 \pm 2$ , and  $13 \pm 2$  nm widths. (b) Differential transmittance through GNRs at a fixed doping level of approximately 0.6 eV normalized to transmittance at the charge neutral point (CNP). (c) Differential transmittance through  $13 \pm 2$  nm wide GNRs as a function of doping level, normalized to transmittance at the CNP. Dashed colored lines indicate regions where the signal strength was small due to absorption in the ionic gel.

perturb the optical properties. We developed a new approach by using a molecular monolayer of pyrene butyric acid (PBA) to alter the surface energy of the graphene (see SI, section S1). This approach leads to large patterned areas with minimal (<2 nm) residue on the patterned graphene surface (see SI, sections S2 and S3), enabling the optical properties of the graphene nanostructures to be unaffected by adventitious surface phonons.

Using this new PBA-based BCP methodology, we fabricated GNRs from CVD-grown graphene<sup>40</sup> on a 525  $\mu$ m Si wafer with 285 nm of thermal oxide. The GNRs were etched in a "zen-garden" pattern with widths ranging from 29  $\pm$  3 nm down to  $12 \pm 2$  nm, as measured using both scanning electron microscopy (SEM) and atomic force microscopy (AFM, see Figure 2a and SI, section S2). The shape and size of the polymer microdomains (and the resultant ribbon dimensions) can be controlled by the molecular weights and relative volume fractions of each block.<sup>41,42</sup> The minimum ribbon width of 12 nm represents the thermodynamic limit of self-assembly for the BCP used in this study, poly(styrene-b-methyl methacrylate), but smaller features are theoretically achievable using more complex BCP compositions.<sup>41,43</sup> In addition to GNRs, we also applied our technique to fabricate nanoperforated graphene, which exhibited optical properties similar to the GNRs (see SI, section S4).

After GNR fabrication, EBL was used to create gold-finger electrical contacts to the sample, and an ionic gel was used to vary the carrier density of the GNRs,<sup>44</sup> as shown in Figure 1b. As-prepared, CVD graphene sheets were hole-doped due to the iron chloride transfer process, with the background Fermi level ( $E_F$ ) ranging from 0.4–0.5 eV (see SI, section S6).<sup>45</sup> The ionic gel gate allowed  $E_F$  to be varied continuously from 0–0.74 eV on ribbons as small as 13 nm.<sup>46</sup> Measurements were also performed using an electrostatic backgate rather than the

ionic gel, including on 12 nm GNRs. Those measurements produced results similar to the ionic gel gate data, however, the  $E_{\rm F}$  could only be varied from 0–0.59 eV, giving a less dynamic range (see SI, section S5). The Fermi level in these experiments was determined through measurements of the interband-transition spectrum of the sample (see SI, section S6).<sup>47</sup> The width and doping-dependent infrared transmission spectra of the GNRs were obtained using a Fourier transform infrared (FTIR) spectroscopy microscope. Doping-dependent transmittance spectra for each sample were normalized to spectra obtained at a Fermi level of 0 eV, the charge neutral point, taken from the same area of the sample.

**Optical Properties of BCP-Fabricated Graphene** Nanoresonators. Infrared spectroscopy measurements of BCP-fabricated GNR devices revealed sharp absorption peaks associated with plasmonic resonances in the GNRs. Figure 2b shows the width-dependent spectra of plasmonic resonances in the GNRs for a constant Fermi level of ~0.6 eV. The wavelength of these resonances shows a distinct blue-shift as the width of GNR dimensions are systematically decreased, which is consistent with previously reported plasmonic resonances in graphene nanostructures.<sup>6,16,19</sup> Variance in the GNR width, as determined by SEM images, is measured to be approximately 2-3 nm, which creates a large fractional change in the width of the smallest features. This effect leads to substantial inhomogeneous broadening in plasmonic resonances for smaller GNRs. Other sources of inhomogeneous broadening may include regions with poor electronic contact and uneven background doping.

Next, we measured the carrier-density dependence of these samples, as shown in Figure 2c for a representative sample with 13 nm wide GNRs. These measurements show that increased doping leads to a blue-shift in the plasmonic resonant frequency and an increase in the intensity of the spectral



**Figure 3.** (a) Theoretical dispersion (lines) of GNR plasmons as a function of ribbon width for various Fermi levels with experimental measurements (symbols) of the resonance energy at specific ribbon widths and Fermi levels. (b) Theoretical (lines) and experimental (symbols) confinement factors of resonant graphene plasmons in GNRs of varying width, plotted for different Fermi energies denoted on the graph. For both (a) and (b), solid lines indicate the local approximation model of graphene, while dashed lines include a nonlocal term. The experimental points are the same measurements across both plots.

features. For the largest achievable doping levels, the resonant energies of the GNRs were observed to occur at SWIR frequencies, well beyond the mid-infrared energies that have been observed in previous experiments. The highest resonant energies that we observed were for 13 nm GNRs with  $E_{\rm F} = -0.73$  eV, where the resonance frequency was tuned to 4500 cm<sup>-1</sup> (2.2  $\mu$ m).

The plasmonic resonances we observe display doping- and width-dependencies that, for large GNR widths, are qualitatively similar to theoretical predictions and experimental measurements.<sup>16,23</sup> However, for narrow (<15 nm) widths, we observe behavior that deviates from theoretical expectations. These behaviors can be observed in Figure 3a, where we plot the resonant frequencies of three representative GNR devices as a function of width for different Fermi levels. For comparison, we also plot the theoretical width-dependent resonant frequencies simulated using a first-order randomphase approximation (RPA) model for the conductivity of graphene<sup>48</sup> and a finite-difference time-domain solver (solid lines). For the widest resonators (purple triangles) there is good agreement between our experiment and theoretical predictions, namely, that the resonances occur at the expected Fermi levels given our uncertainties. However, our measurements reveal that, when the GNR width is decreased below 15 nm, the plasmonic resonances are blue-shifted from first order RPA-based calculations.<sup>48</sup> For example, Figure 3a shows that 13 nm wide GNRs with an  $E_{\rm F}$  of 0.71 eV display a resonance near 4500 cm<sup>-1</sup>, while first-order RPA predicts the resonance to occur near 3600 cm<sup>-1</sup>, an offset of more than 20%. In order to match the theoretical curves of the first-order RPA model, the widths of the GNRs would need to be nearly half the widths measured using SEM (see SI, section S2), or the carrier density would need to be at least 30% more than what we

estimate based on the experimentally measured interband transition cutoff (see SI, section S6). Both scenarios are unlikely based on our experimental uncertainty.

We can further analyze the properties of these plasmonic modes by calculating their confinement factors, the ratio of the free-space wavelength to the plasmon wavelength.  $(\lambda_0/\lambda_p)$ . We extracted the plasmonic wavelength through our simulations, where the plasmonic resonators behave as Fabry–Perot oscillators with a nontrivial edge scattering phase.<sup>16</sup> The resulting confinement factors are shown in Figure 3b for different ribbon widths and doping levels. We found that our smallest ribbons, 13 nm wide GNRs, featured confinement factors as large as 137 ± 25. This value is 25% higher than what has previously been achieved in 20 nm wide GNRs,<sup>16</sup> and within a margin of error of the largest observed confinement factor in an optical cavity of a 2D material, which was demonstrated using vertically confined acoustic graphene plasmons.<sup>34</sup>

## DISCUSSION

Our results reveal that the behavior of graphene plasmons strongly deviates from first-order optical models at SWIR frequencies, and that this deviation manifests as a blue-shift in the characteristic frequency of graphene plasmonic resonances. We believe that the large blue-shifts that we observe in narrow GNRs are not due to potential experimental errors, but rather can be understood as nonlocal and electron-quantization effects perturbing the graphene plasmons,<sup>35–37,49</sup> as described below.

Optical nonlocality describes the effect of an electric field in one location producing a polarization in the nearby vicinity. Such perturbations are known to occur most strongly in regions of high optical field enhancement, as in metallic nanostructures with small (<10 nm) geometric features.<sup>50,51</sup> These effects can be described mathematically as a modification to Ohm's Law, by connecting the in-plane currents I and electric fields E as follows:  $I = \sigma(\omega)E$  –  $\frac{\beta^2}{c^2} \nabla(\nabla \cdot J)$ , where  $\sigma(\omega)$  is the conductivity of graphene and the  ${\beta}^2$  term accounts for the pressure of an inhomogeneous electron fluid, representing the approximation of the nonlocal effects in a semiclassical approach.<sup>35</sup> In order to determine the magnitude of the shift of the plasmonic resonances in our GNR devices due to nonlocality, we included this modification to Ohm's law to our finite element Maxwell equation solver (COMSOL) simulations of the GNRs.<sup>35,51</sup> The plasmonic behavior was modeled by electromagnetic waves scattering off the GNRs, which created resonances in the transmission spectra. The results of those calculations (shown in Figure 3a,b as dashed lines) indicate that nonlocal effects blue-shift the resonant plasmon energies in GNRs and that this effect is more dramatic as the ribbon width is decreased and for lower doping levels. For example, for 29 nm GNRs at  $E_{\rm E}$  = 0.73 eV, nonlocal effects shift the resonant frequency by 2%, while for 13 nm wide GNRs at  $E_{\rm F}$  = 0.71 eV, the resonant frequency is shifted by 12%. While these corrections bring the theoretical predictions closer to the 20% shift we observed in our experiment, they do not fully account for the total blue-shift.

A second possible contribution we consider is electron quantization in the GNRs, where the continuum model for graphene quasiparticles breaks down, forming low-energy band gaps and exotic edge states that depend on the exact edge termination of the GNRs.<sup>52-57</sup> Such effects become stronger for more narrow GNRs, and calculations from ref 37 indicate that quantum effects should blue-shift the plasmonic resonance of 13 nm wide GNRs by approximately 5%.<sup>36,37</sup> The prospect of electron quantization occurring in these devices is supported by transport measurements performed on similarly prepared NPG samples with characteristic widths of  $18 \pm 2$  nm.<sup>3</sup> <sup>2</sup> Those measurements revealed an effective electronic bandgap of 100 meV, which could strongly perturb the infrared graphene dielectric properties and drive changes in the resonant plasmonic response.

The combined effects of optical nonlocality and electron quantization, evaluated independently, account for the majority of the experimentally observed blue shifts in our measurements, but they do not completely describe the offsets that we observe. The remaining discrepancies could potentially be due to GNRs that have effective widths that are slightly thinner than what we observed in SEM/AFM measurements caused by, for example, damaged graphene edges due to RIE undercutting (see SI, section S2). We also note that a complete theoretical model should consider both optical nonlocality and electron quantization effects concurrently and should include additional effects such as band renormalization and Landau damping.<sup>58</sup> Such a model is beyond the scope of this work and left to future investigation.

The blue-shift in the resonance frequency that we observe has broad implications for the limits of future optoelectronic devices based on graphene plasmons. Most importantly, our results reveal that graphene nanostructures can exhibit a strong, tunable optical response in the SWIR. Moreover, the length scales needed to realize such behavior are larger than previously predicted and directly accessible to BCP lithography. For example, our first-order RPA calculations indicated that to show plasmonic activity at telecommunication

frequencies (1.55  $\mu$ m), GNR widths of 4.5 nm at a carrier density of 1 eV would be necessary, requiring significant advances in large-scale fabrication techniques. However, because nonlocal and quantum perturbations increase in magnitude as GNR width is decreased, it may be possible to reach telecommunication frequencies in GNRs with widths of 7-10 nm, requiring only modest improvements over the fabrication methods described in this work. Another important consequence of the blue-shift that we observe is that the confinement factors of graphene plasmons with short wavelengths are smaller than previously predicted, as illustrated in Figure 3b.<sup>20</sup> This decrease in confinement indicates that several predicted phenomena that leverage graphene plasmondriven light-matter interactions, including SPASing,<sup>59</sup> enhanced spontaneous emission of forbidden transitions,<sup>25</sup> and enhanced sensing,<sup>5</sup> may occur at lower rates than previously anticipated. For example, 13 nm GNRs were previously calculated<sup>20</sup> to exhibit a confinement factor of ~120 with an  $E_{\rm F}$ of 0.64 eV in comparison to the 84  $\pm$  13 confinement factor we observed in this work for an  $E_{\rm F}$  of 0.63 eV. Since twoplasmon spontaneous emission rates scale as  $(\lambda_0/\lambda_p)^{6,25}$  our results indicate emitters coupled to such GNRs will undergo two-plasmon spontaneous emission at a rate 1 order of magnitude lower than previously thought.

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In conclusion, we developed a fabrication technique based on block copolymer (BCP) lithography that allowed us to probe new regimes of graphene plasmonics and enabled the first measurement of resonant graphene plasmons in the shortwavelength infrared (SWIR). Our results provide direct evidence that scaling laws of graphene plasmons change at sub-15 nm length scales. These changes correlate with the modeled predictions of both nonlocal and electron quantization effects. Consequently, reaching the SWIR wavelengths, and even shorter, can be achieved in larger structures than previously thought, facilitating a new avenue of research for graphene-based devices. The graphene nanostructures we fabricated also exhibit, to the best of our knowledge, among the largest lateral confinement factors as 2D optical cavities in the literature.<sup>34,60-63</sup> However, these results demonstrate that confinement is actually smaller than previously predicted,<sup>20</sup> limiting the anticipated ability of graphene to enhance lightmatter interactions. Our findings show that graphene plasmonic devices created using BCP lithography represent an exciting platform to expand the tunable working range of graphene plasmonics, enhance light-matter interactions, explore quantum effects, and create new types of graphene devices.

#### METHODS

**Graphene Chemical Vapor Deposition (CVD) Growth.** Graphene was grown by CVD methods on low purity Cu foil (15465015, Alfa Aesar). Cu foil was precleaned with a 30 s 3:1 deionized water/ammonium persulfate dip (APS – 100, Transene). Graphene was grown at 1035 °C for 90 min, while 42 sccm H<sub>2</sub> and 0.2 sccm CH<sub>4</sub> (both Air Gas Research 6.0 grade) flowed in the quartz growth tube (260 mTorr). To transfer the graphene after growth, graphene was first coated with a protective layer of PMMA (950k A4, MicroChem Corp.), and the Cu foil was etched away with FeCl<sub>3</sub> (CE – 100, Transene). The graphene/PMMA stack was then rinsed in a series of deionized water baths. Si/SiO<sub>2</sub> substrates (double side polished, 285 nm dry thermal oxide, prime grade Si wafers from WaferPro) were piranha-treated using 3:1  $H_2SO_4/H_2O_2$  at 85 °C for 30 min immediately prior to graphene/PMMA transfer. Once transferred, the PMMA was removed by soaking in 60 °C acetone for 1 h, and the graphene/SiO<sub>2</sub> was annealed for 1 h at 400 °C under 10<sup>-6</sup> Torr vacuum.

Nanoribbon and Nanoperforated Graphene Fabrication. The monolayer graphene-coated SiO<sub>2</sub> substrates were placed in a 1-pyrenebutyric acid (PBA; 257354, Sigma-Aldrich) solution in THF for 24 h based on a previously developed procedure.<sup>64</sup> A random copolymer (RCP) of glycidyl methacrylate (GMA), styrene (S), and methyl methacrylate (MMA), P(S-r-MMA-r-GMA), was synthesized as reported earlier.<sup>65</sup> For this study, the RCP contained 62.5% S, 4% GMA, and balance PMMA (as confirmed by NMR) for lamellar forming BCPs. For cylindrical BCPs, the RCP contained 72% S, 4% GMA, and balance PMMA. The RCP was dissolved in toluene (320552, Sigma-Aldrich) and spin coated on the PBA-coated graphene/SiO<sub>2</sub> substrate. These samples were annealed at 160 °C for 3 h under vacuum to cross-link the GMA unit and soaked in toluene for 15 min to remove any unreacted RCP. We used BCP P(S-b-MMA) with various molecular weights (MWs) all from Polymer Source, Inc., specifically 17k-17k and 53k-54k MWs for lamellarforming PS-b-PMMA and 21.5k-10k MW for cylindricalforming PS-b-PMMA. These BCPs were prepared in toluene and spin coated onto the random copolymer covered samples. Films were thermally annealed under vacuum for BCP selfassembly. Pattern transfer from the BCP to the underneath graphene was performed using a reactive ion etcher (Plasma-Therm 790) with oxygen plasma. Scanning electron microscope (SEM) images were taken with a Zeiss LEO 1550VP SEM for nanopatterned graphene visualization. Back-gatedonly NPG samples were fabricated with a slightly modified fabrication procedure described in detail in SI, section 4. Additional samples were prepared using these procedures that exhibited optical behavior similar to what was reported in the main text.

Fabrication of Gold Contacts. For the GNR-coated  $SiO_2/Si$  substrates, they were first coated with a bilayer PMMA (950 A4 at 200 nm and 495 C2 at 300 nm). These samples were then exposed and patterned using the Elionix ELS G-100, an electron-beam lithography tool. After exposure, the substrates were developed in a 3:1 IPA/DI water mixture for 20 s with a 10 s rinse of IPA. Metal deposition consisted of a 2.5 nm chromium adhesion layer and 80 nm of gold. After deposition, the PMMA was removed via a 15 h chloroform bath, a 1 h acetone bath, and then a 5 min IPA bath with a 5 s IPA rinse. The contacts for the GNRs were a gold-electrode mesh of interlocking branches that are 80 nm wide and spaced by 3  $\mu$ m. This pattern ensures reliable contact to the graphene nanoribbons in the "zen-garden" pattern without significantly reducing the optical signal or introducing additional resonances in the wavelength range of interest  $(2-6 \ \mu m)$ . For NPGs, the graphene remained a continuous sheet, so large gold contacts were applied via metal deposition through a mask.

**lonic Gel Preparation.** Ionic gel preparation based on previously established procedure in literature.<sup>46</sup> Diethylmethyl-(2-methoxyethyl)ammonium bis(trifluoromethylsulfonyl)imide ([DEME][TFSI]) was purchased from Sigma-Aldrich Chemicals. Initially, the ionic liquid was dried at 105 °C under vacuum for 3 days. Polystyrene-*b*-poly(ethylene oxide)-*b*-polystyrene (PS-*b*-PEO-*b*-PS) triblock copolymer was purchased from Polymer Source, Inc. The molecular weight of the block copolymer was PS 10 kg/mol, PEO 44 kg/mol, and PS 10 kg/mol, which corresponds to a PEO volume fraction of 0.67. A total of 0.55 g of [EMIM][TFSI] was dissolved with 21 mg of PS-*b*-PEO-*b*-PS in 2 mL of anhydrous dichloromethane. The solution was stirred overnight at room temperature. The ionic gel was spin-coated on the graphene sample and stored under N<sub>2</sub> until ready for use.

**FTIR Measurements.** The transmission measurements were performed using a Bruker Vertex 70 FTIR attached to a Hyperion 2000 microscope in a nitrogen-purged environment. We used a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector. For our plasmonic resonance measurements, we used a potassium-bromide (KBr) beam splitter with a silicon carbide glow bar as our MIR source. For the measurements of the Drude peaks (see SI, section S6), we used a quartz beam splitter with a halogen bulb as our source.

Electromagnetic Simulations. We rigorously solved Maxwell's equations using both a finite-difference time-domain (FDTD) method and a finite-element method (FEM). While these methods give the same result for the local calculations, the FDTD solver could not incorporate nonlocal corrections, so we used the FEM solver for the nonlocal calculations. Graphene was modeled as a thin material of thickness  $\delta$  with permittivity  $\epsilon_{\rm G} = \epsilon_{\rm r} + \frac{i\sigma(\omega)}{\epsilon_0\omega\delta}$  is the complex optical conductivity of graphene evaluated within the local random phase approximation.<sup>48</sup>  $\delta$  was chosen as 0.3 nm which showed good convergence with respect to the  $\delta \rightarrow 0$  limit and  $\epsilon_r$  is the background relative permittivity. For the FDTD simulations, we used the commercial solver Lumerical FDTD. The graphene nanostructures were simulated on an SiO<sub>2</sub> layer with a thickness of 285 nm, on top of a Si substrate. Material properties from Palik<sup>66</sup> were used for both materials. To model the structure accurately, we included a polymer layer of thickness 1.2 nm, with dielectric properties taken as average of PMMA<sup>67</sup> and PS.<sup>68</sup> Our simulations of the nonlocal effect made use of the FEM solver COMSOL Multiphysics. We made use of the NanoPL RF module,<sup>51</sup> an extension designed for calculating nonlocal effects of 2D nanostructures. Graphene was modeled identically to the FDTD approach and an average background dielectric of 2.5 was used to represent the contributions of the dielectrics surrounding the graphene to estimate the shift caused by the nonlocal effects.

## ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsphotonics.1c00149.

Discussion of the following: Block copolymer choice and pyrenebutryic acid interfacial layer; Calculating width of graphene nanoribbons; Removing polymer mask; Fabrication and measurement of nanoperforated graphene; Electrostatic gating to tune the Fermi level of samples; Measuring Fermi levels; Modeling reduced plasmon dispersion; Comparison of simulated spectra to measured spectra (PDF)

## AUTHOR INFORMATION

#### Corresponding Author

Victor W. Brar – Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; Email: vbrar@wisc.edu

### Authors

- Joel. F. Siegel Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; © orcid.org/0000-0002-7344-4839
- Jonathan H. Dwyer Department of Chemical and Biological Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Anjali Suresh Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Nathaniel S. Safron Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Margaret A. Fortman Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Chenghao Wan Department of Materials Science and Engineering and Department of Electrical and Computer Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; orcid.org/0000-0002-4132-4779
- Jonathan W. Choi Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Wei Wei Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Vivek Saraswat Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Wyatt Behn Department of Physics, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; © orcid.org/0000-0003-1377-5502
- Mikhail A. Kats Department of Physics, Department of Materials Science and Engineering, and Department of Electrical and Computer Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; • orcid.org/0000-0003-4897-4720
- Michael S. Arnold Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States
- Padma Gopalan Department of Chemical and Biological Engineering and Department of Materials Science and Engineering, University of Wisconsin–Madison, Madison, Wisconsin 53706, United States; orcid.org/0000-0002-1955-640X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsphotonics.1c00149

#### **Author Contributions**

<sup>#</sup>J.F.S. and J.H.D. contributed equally to this work. M.F., N.S.S., and V.S. grew graphene. J.H.D., A.S., J.W.C., and W.W. fabricated graphene nanostructures with block copolymer lithography procedures. J.H.D., J.W.C., and N.S.S. performed SEM imaging. J.H.D. and A.S. characterized graphene nanostructure size with SEM images. W.A.B. performed AFM imaging and graphene nanostructure size analysis with AFM images. J.F.S. fabricated electrical leads on graphene nanostructures. J.F.S. and C.W. performed FTIR measurements and analysis. J.F.S. performed electromagnetic simulations. J.F.S. and J.H.D. lead manuscript preparation, with contributions from all authors. V.W.B., P.G., M.A.K., and M.S.A. supervised this research project.

#### Notes

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