

Graphene-metamaterial photodetectors for integrated infrared sensing

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ABSTRACT In this work we study metamaterial enhanced graphene photodetectors operating in the mid-IR to THz. The detector element consists of a graphene ribbon embedded within a dual-metal split ring resonator, which acts like a cavity to enhance the absorption of electromagnetic radiation by the graphene ribbon, whilst the asymmetric metal contacts enable photo-thermoelectric detection. Detectors designed for the mid-IR demonstrate peak responsivity (referenced to total power) of $\sim 120\text{mV/W}$ at 1500cm^{-1} and are employed in the spectroscopic evaluation of vibrational resonances, thus demonstrating a key step towards a platform for integrated surface enhanced sensing.

Infrared (IR) spectroscopy is a powerful analytical technique that can be used to gain information about the chemical makeup of almost any sample in almost any state¹. A molecular bond will absorb IR light as long as it has vibrational modes which change the electric dipole moment of the bond, and IR spectroscopy is therefore widely used across different scientific disciplines. As IR spectroscopy is both non-destructive and label-free, it is particularly attractive for the analysis of biological samples such as proteins², lipids³ and bacteria⁴. In particular, Fourier transform infrared (FTIR) spectroscopy allows the rapid, and highly sensitive, measurement of transmission and reflection spectra. However, the large mismatch between the wavelength of light and the size of the sample of interest limits both the spatial resolution and sensitivity of such measurements.

One way to overcome this mismatch is to exploit the localized light fields associated with surface plasmon polaritons (plasmons) excited in nanostructures⁵. At mid-infrared (mid-IR) wavelengths and longer, surface plasmons are weakly bound to the metal-dielectric interface. Nevertheless, plasmonic nanostructures⁶, metamaterials⁷ and tapered waveguides⁸ have been employed to confine the electric-field to sub-wavelength volumes and significantly enhance the light matter interaction. In contrast to noble metals, graphene has been shown to support tightly confined surface plasmon (SP) in the THz to mid-IR spectral range^{9,10}, with the significant advantage that the plasmon resonance can be tuned by changing the conductivity of graphene, which in turn can be modulated using an applied gate voltage. In very recent work, graphene plasmonic resonators have been demonstrated as an effective sensing platform^{11,12}, where the tunability and strong spatial light confinement offer a tangible improvement over conventional plasmonic devices for the mid-IR sensing of protein monolayers¹².

In this work we exploit a hybrid graphene metamaterial¹³ as means of significantly enhancing the interaction of IR light with the sample under test, but also integrate this metamaterial with graphene photodetectors¹⁴ operating in the IR to THz. We show that the metamaterial enhances the response of the detectors, measure a peak responsivity of $>100\text{mV/W}$ (defined with respect to the incident power falling on the whole area of the detector) at a frequency of $\sim 1500\text{cm}^{-1}$ and determine that the photo-response is dominated by the photo-thermoelectric effect. Using the integrated detector we are able to reproduce the transmission spectrum of a very thin ($\sim 20\text{nm}$) layer of test polymer, where features associated with the vibrational modes within the polymer molecules appear as minima in the measured photo-voltage. This is a key step towards the realization of a fully integrated, high spatial resolution, surface enhanced sensor and ultimately could form the basis of a spectrometer-on-a-chip.

The concept of our device is pictured in Fig. 1(a) and (b) and consists of a graphene ribbon positioned in the capacitor gap of a complementary split ring resonator (CSRR), which is also split along its horizontal symmetry axis¹³. The upper and lower sections of the CSRR are in direct contact with the graphene ribbon and composed from different metals, Cr/Au (5/80nm) for the lower section and Al (90nm) for the upper section. Using these two different metals has little effect on the electromagnetic response of the CSRR (see supporting information), but the asymmetry of the two graphene-metal interfaces facilitates photo-thermoelectric detection¹⁵. Fermi-level pinning at the graphene-metal interfaces breaks the symmetry of the carrier density and therefore Seebeck coefficient along the graphene channel, leading to the generation of a net thermoelectric voltage. Detector arrays with an area of $600\times 600\mu\text{m}^2$ consist 120×120 individual detector elements connected in parallel along the x-axis and in series along the y-axis as shown

in Fig. 1(a), with source and drain contacts to allow read-out of the photo-voltage and for electrical characterization of the device. In the following, we present experimental results from devices operating in two different frequency ranges. The first device, D1 targets an enhanced response in the THz range and operates across a broad frequency range. The second, D2 is designed for mid-IR operation, the optimum frequency range for vibrational spectroscopy, and is measured with and without a ~20nm thick layer of Poly(methyl methacrylate) (PMMA) in order to investigate surface enhanced sensing. The IR spectrum of PMMA, a versatile polymeric material, has well known molecular absorption lines at 1730cm^{-1} (corresponding to C=O stretching), 1450 and 1380cm^{-1} (O-CH₃ bending), 1265cm^{-1} and 1240cm^{-1} (C-C-O stretching), 1190cm^{-1} (C-O-C bending), and 1145cm^{-1} (CH₂ bending) and therefore provides an excellent test system^{1,16}.

The detector photo-response is measured using the experimental set-up shown in Fig. 1(c). The broadband radiation from the FTIR is passed through a chopper wheel and a linear polarizer and then focused onto the detector (mounted inside a vacuum chamber with a KRS-5 window) using a reflective objective lens (N.A.=0.5). The photo-voltage generated between the source and drain contacts of the detector is amplified using a voltage preamplifier and measured with a lock-in amplifier referenced to the chopper frequency (~500Hz). The lock-in output voltage is then recorded as a function of the FTIR interferometer delay to record an interferogram of the detector response, the Fourier transform of which gives the spectral response of the system, i.e. the photo-voltage generated due to the power spectrum of the FTIR thermal source. To quantify the performance of the detector, the photo-response is normalized to the power spectrum of the FTIR source using a calibrated Mercury Cadmium Telluride detector with a known spectral

response (see supporting information). The response of D2 is further characterized using a quantum cascade laser (QCL) with a fixed frequency of $\sim 1200\text{cm}^{-1}$, which has a focused beam diameter of $\sim 60\mu\text{m}$ (measured using a micro-bolometer array), considerably smaller than the detector area, and an average power of $\sim 8\text{mW}$.

To characterize the electromagnetic response of the hybrid metamaterial detectors, we first use FTIR spectroscopy to measure the transmission spectrum of the CSRR array (without graphene ribbons). When the incident radiation is polarized with the electric-field perpendicular to the long-axis of the graphene ribbon, in the corresponding hybrid structure (see Fig. 1(a) for orientation), the spectrum, shown in Fig. 1(d) reveals several peaks within the measurement frequency range of 100 to 1800cm^{-1} . In the orthogonal polarization, with the electrical field parallel to the long-axis of the graphene ribbon and also shown in Fig. 1(d), we observe a very different spectral response. In both cases, the spectra can be attributed to the interaction of the resonant modes of the CSRR with the optical phonons of the underlying SiO_2 substrate¹⁷. This can be shown by calculating the expected electromagnetic response using finite difference time domain (FDTD) simulations, where the optical phonons are included using a frequency dependent dielectric function of the SiO_2 layer (see supporting information). Calculated transmission spectra are plotted for comparison in Fig. 1(e) and show good agreement with the experimental measurements.

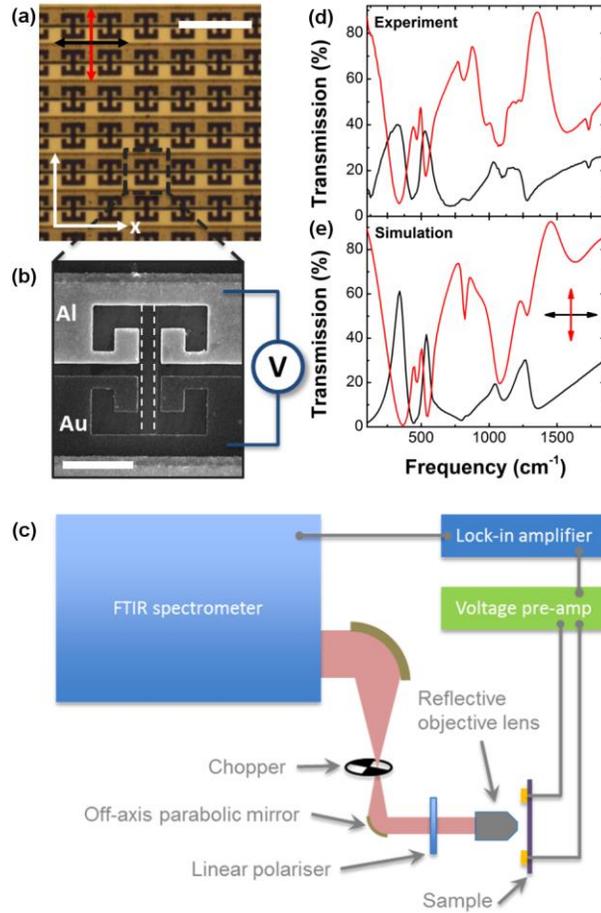


Figure 1. (a) Optical micrograph and (b) Scanning electron microscope image of the hybrid metamaterial detector. The red and black arrows in (a) denote polarization parallel and perpendicular to the graphene ribbon, respectively. The dashed white lines in (b) indicate the edge of the graphene ribbon. The scale bar is $10\mu\text{m}$ in (a) and $2\mu\text{m}$ in (b). (c) Schematic diagram of the experimental set-up. (d) Experimental and (e) FDTD simulated transmission spectra of the CSRR array without graphene ribbons. In (d) and (e) the black and red lines represent the case of perpendicular and parallel polarized excitation, respectively.

We then measure the photo-response of detector D1, which is presented in Fig. 2. Firstly, we consider the response to radiation polarized perpendicular to the graphene ribbons. The photo-response spectrum is shown in Fig. 2(a), recorded with $V_G \approx V_{\text{CNP}}$ (where V_{CNP} is the bias voltage

corresponding to the charge neutral point). There are three main features; a broad response peak between 1500 and 4000 cm^{-1} , and two narrow response peaks at ~ 530 and 1250 cm^{-1} . The transmission spectrum for the perpendicular polarization is plotted in Fig. 2(b) for comparison and it can be seen that, in general, the photo-voltage maxima correspond to the transmission maxima (the lowest frequency resonance, at $\sim 300\text{cm}^{-1}$, is not observed in the photo-response because the KBr beamsplitter used in the FTIR has a cut-off frequency of 400 cm^{-1}). A similar observation is made when the polarization is parallel to the graphene ribbon, as shown in Figures 2(c) and 2(d), but with a different frequency response.

A correlation between the transmission and photo-response spectra can be expected for our detector design if the CSRR confines the electric field from the incident radiation within the capacitor gap, therefore enhancing absorption within the graphene ribbon. To investigate this, we use the FDTD simulations to visualize the electric field profiles at the different resonant frequencies of the CSRR, shown for perpendicularly polarized light of three frequencies in Fig. 2(e) – Fig. 2(g). Enhancement of the photo-response is observed at frequencies of 530 cm^{-1} and 1250 cm^{-1} , which results from the strongly enhanced electric field within the capacitor gap of the CSRR as shown in Figures 2(e) and (g), respectively. In both polarizations however, there are resonant modes which occur in the transmission spectra but not the photo-response, for example in the perpendicular polarization there is no peak in photo-response corresponding to the mode at 1035 cm^{-1} . Referring again to the FDTD simulations, we observe that in this case the resonant mode does not significantly enhance the electric field within the capacitor gap (Fig. 2(f)). These observations provide strong evidence that the photo-response is dominated by absorption of radiation by the graphene ribbon and enhanced by the CSRR.

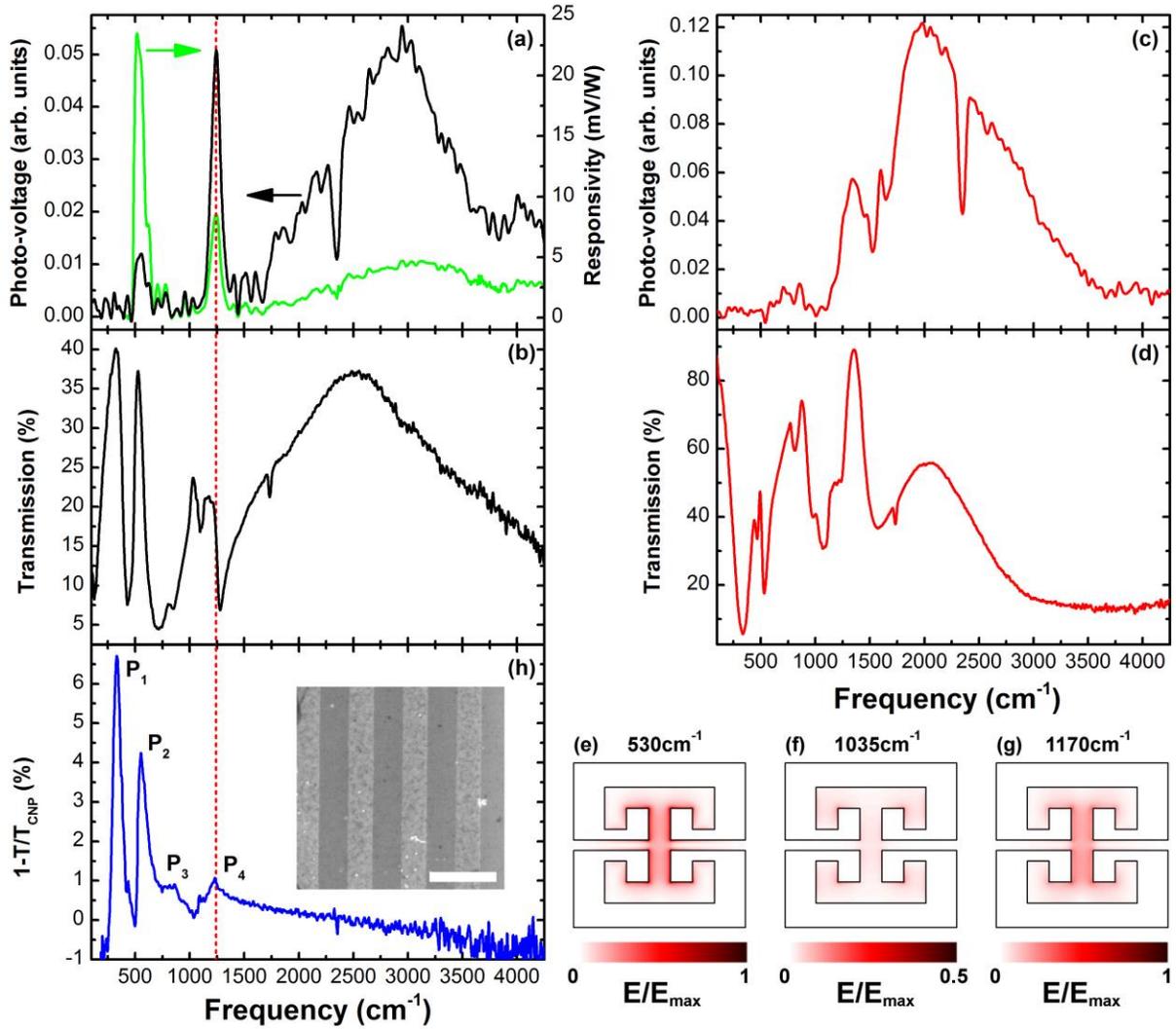


Figure 2. (a, c) Photo-voltage spectra of the hybrid metamaterial detector in response to excitation with (a) perpendicular and (c) parallel polarized light. The green line in (a) shows the calibrated response spectrum. (b, d) Transmission spectra of the metamaterial array with (b) perpendicular and (d) parallel polarization. (e) – (g) Simulated electric field profile of the CSRR for perpendicular polarization at frequencies of (e) 530cm^{-1} , (f) 1035cm^{-1} and (g) 1170cm^{-1} . (h) Extinction spectrum of an array of 400nm wide monolayer graphene ribbons, the plasmon-phonon modes are labelled P_1 - P_4 . Inset shows an SEM image of graphene ribbon array, the scale bar is $1\mu\text{m}$. The red dashed line in (a), (b) and (h) indicates the frequency of the plasmon-phonon resonance in the graphene ribbon.

We also note that the resonance in the photo-response at 1250cm^{-1} is significantly narrower than the transmission resonance. This is attributed to an enhanced absorption in the graphene ribbon as a result of plasmon-phonon coupling^{18,19}. The extinction spectrum ($1-T/T_{\text{CNP}}$, where T is the transmission through the ribbon array biased to give a hole density of $\sim 1 \times 10^{13}\text{cm}^{-2}$ and T_{CNP} is the transmission through the array biased to the charge neutral point) of an array of 400nm wide graphene ribbons (see inset to Fig. 2(h) for SEM image) is shown in Fig. 2(h) and shows resonant modes, labelled P_1 - P_4 , resulting from increased absorption due to the hybridization of the plasmon resonance in the graphene ribbons with optical phonons in the underlying SiO_2 substrate¹⁹. The plasmon-phonon mode at 1250cm^{-1} , labelled P_4 , overlaps in frequency with the CSRR mode centered at 1170cm^{-1} , which concentrates the field within the capacitor gap, thus coupling to the graphene plasmon-phonon resonance¹³ and the enhanced absorption associated with this resonance is observed as a peak in the thermoelectric voltage²⁰. This observation is supported by the linewidth of the plasmon-phonon mode, which is $\sim 110\text{cm}^{-1}$, in close agreement with the $\sim 105\text{cm}^{-1}$ measured linewidth of the photo-response peak. The responsivity of D1 is plotted in Fig. 2(a) for the perpendicular polarization. A peak responsivity of 23mV/W is measured at 530cm^{-1} , corresponding to the LC resonance of the CSRR. Similarly, for the cavity enhanced plasmon-phonon mode at 1250cm^{-1} the responsivity peaks at $\sim 9\text{mV/W}$.

We now move onto D2 and show that the combination of metamaterial with graphene detection can form the basis of an integrated sensor for surface enhanced molecular spectroscopy. D2 is designed for operation in the mid-IR with the ribbon width reduced to 200nm and the CSRR dimensions scaled to give an LC resonance at $\sim 1500\text{cm}^{-1}$ (see inset of Fig. 4(c) for SEM image). The polarization sensitive photo-response spectra are plotted in Fig. 3(a), which result from the near-field enhancement of the CSRR modes, as seen previously. When the

polarization is perpendicular to the graphene ribbon the photo-response is dominated by the LC mode of the CSRR, which hybridizes with a SiO₂ surface phonon mode resulting in a pair of narrow resonances at ~ 970 and 1550cm^{-1} . Calibrating the response of this detector with the procedure outlined above results in a maximum responsivity of $\sim 110\text{mV/W}$, as shown in the inset to Fig. 3(a).

Fig. 3(b) plots the responsivity of D2 to the QCL with fixed frequency of $\sim 1200\text{cm}^{-1}$ as a function of gate bias, which peaks at $\sim 12\text{mV/W}$ close to the charge neutral voltage, in good agreement with the FTIR response measurement which gives a responsivity of 13mV/W at 1200cm^{-1} (see inset to Fig. 3(a)). The gate characteristic is used to identify the dominant detection mechanism as the photo-thermoelectric effect arising from the asymmetric metal contacts^{15,21,22}. Using the FDTD simulated electric field enhancement (see inset to Fig. 3(b)) and a one dimensional finite element model of the carrier density and temperature distribution along the graphene channel, good qualitative agreement is found between the experimental results and the simulated responsivity, as shown in Fig. 3(b) (see supporting information for simulation details). Assuming a Johnson noise floor of $\sim \sqrt{4K_BTR}$, where R is the resistance, the room temperature noise equivalent power (NEP) can be estimated as $\sim 200\text{nW/Hz}^{1/2}$. However, the measured responsivity of the detector array is two orders of magnitude smaller than for a single unit cell, due to the parallel connection of the columns of detector unit cells (see supporting information). Therefore, we estimate that the responsivity of a single unit cell should peak at $\sim 1.5\text{V/W}$ at 1200cm^{-1} , in good agreement with the simulated value shown in Fig. 3(b), and a maximum of $\sim 10\text{V/W}$ at 1550cm^{-1} . This leads to a room temperature NEP of the detector unit cell of $\sim 2\text{nW/Hz}^{1/2}$.

To investigate surface enhanced sensing with the hybrid metamaterial detector, we deposit a $\sim 20\text{nm}$ thick layer of PMMA directly on to the detector surface and Fig. 3(c) shows the modified photo-response spectra of the detector. The detector incorporates two sensing mechanisms; refractive index sensitivity, and the resonant coupling of molecular vibrations to the modes of the CSRR. Firstly, the modification of the dielectric constant in the vicinity of the CSRR results in a red-shift of the resonant modes. This is clearly observed by comparing the resonant frequencies of the LC mode with (Fig. 3(c)) and without (Fig. 3(a)) the PMMA layer. The shift of $\sim 150\text{cm}^{-1}$, $\sim 10\%$ of the resonant frequency, compares well to the refractive index sensitivity demonstrated with graphene plasmonic resonators^{11,12}. Secondly, as shown by the photo-response spectra in Fig. 3(c), for both parallel and perpendicular excitation the detector response is modified by the coupling of the resonant modes of the CSRR to the vibrational modes of the PMMA molecules. This coupling results in sharp features, which can be identified from the known vibrational resonances of PMMA as labelled in Fig. 3(c). Particularly clear are the C=O stretch mode at $\sim 1730\text{cm}^{-1}$ and the bending vibration of the O-CH₃ bonds at $\sim 1450\text{cm}^{-1}$ (ref. 1). The dip in photo-voltage corresponding to the frequency of the vibrational modes represents a decrease in absorption due to the destructive interference of two mutually coupled excitations in a process known as plasmon-induced transparency¹¹.

The number of C=O bonds, within the detection volume of a single CSRR is estimated to be ~ 20 attomole, following the procedure outlined by Adato *et al.*²³ and assuming a molecular density of 1.17g/cm^3 and mass of 100g/mol . The difference in the responsivity of the detector with and without the PMMA layer is estimated from Fig. 3 to be $\sim 1.2\text{V/W}$ for a single unit cell,

which gives a change in responsivity, $\Delta\mathcal{R}$ of $7.2 \times 10^{16} \text{V/Wmol}$. From the ratio of the Johnson noise and the change in responsivity, we then estimate an equivalent measurement noise ($\sqrt{4K_B TR}/\Delta\mathcal{R}$) of $\sim 3 \times 10^{-25} \text{Wmol/Hz}^{1/2}$. This equivalent measurement noise describes the power that is required to be incident upon a single unit cell for the detection of 1 mol of material with a S/N ratio of 1 in 1Hz bandwidth. Or, in other words, a power of $\sim 0.3 \text{mW}$ is required for a detection sensitivity of 1 zeptomol.

Finally, Fig. 3(c) shows that the resonant response of the detector is polarization dependent, with the perpendicular polarization covering the frequency range $600\text{-}2000 \text{cm}^{-1}$ and the parallel polarization $1100\text{-}3000 \text{cm}^{-1}$. This polarization sensitivity can provide an additional degree of freedom in identification of unknown molecules, which is highlighted by the detection of the C-H stretch mode at $\sim 2900 \text{cm}^{-1}$ in the photo-response spectrum to parallel polarization (Fig. 3(c)).

In conclusion, we have demonstrated cavity enhanced graphene based photo-thermoelectric detectors spanning the mid-IR and THz frequency range, with broadband operation and resonant enhancement. Furthermore, the strong enhancement of the electric field combined with the electrical read-out can be used in the detection and identification of surface adsorbed molecules, which has potential for integrated surface enhanced sensing. An increase in responsivity of 1-2 orders of magnitude can be expected if a p-n junction is created in the graphene channel. This can be achieved by differentially doping the two halves of the graphene channel using buried or top gates or with a selective doping process, such as electron beam irradiation²⁴. Importantly, this would also enable high responsivity at high carrier density in the absorption region^{21,25} and therefore be compatible with enhanced absorption due to plasmonic resonances^{10,18,19} and strong

coupling of the hybrid metamaterial¹³. The tunability of the hybrid modes¹³, also provides a route towards spectrometer free sensing²⁶, which combined with the integrated detector opens up the possibility of highly sensitive, low cost and miniaturized sensors for point-of-care medical applications.

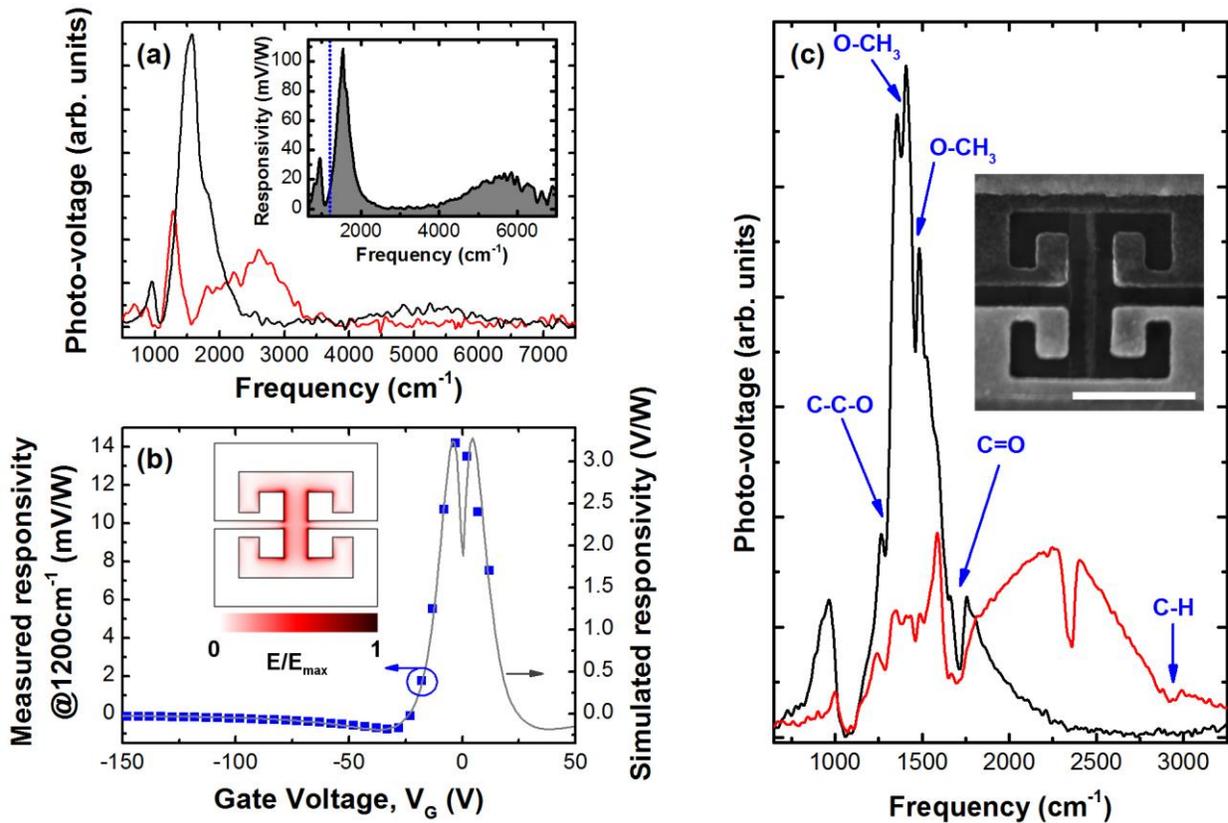


Figure 3. (a) Photo-voltage spectra of hybrid metamaterial detector designed for mid-IR. The inset to (a) shows the calibrated response spectrum of the detector to perpendicular polarized light and the dotted blue line indicates the frequency of the QCL. (b) Experimental and calculated responsivity for the metamaterial enhanced graphene detector as a function of gate voltage. The inset to (b) shows the calculated electric field profile of the CSRR at the QCL frequency of 1200cm^{-1} . (c) Photo-voltage spectra of the mid-IR hybrid metamaterial enhanced graphene detector with $\sim 20\text{nm}$ thick coating of PMMA. In (a) and (c) the black (red) line shows the response to excitation

with perpendicular (parallel) polarized light. The strong absorption line at $\sim 2400\text{cm}^{-1}$ is a result of atmospheric CO_2 absorption. The inset to (c) shows an SEM image of a single unit cell of the detector and the scale marker is $1\mu\text{m}$.

ASSOCIATED CONTENT

Supporting Information FDTD simulation details, including Lorentz model of SiO₂ permittivity; calibration of FTIR-measured photo-response; details of photo-thermoelectric photoresponse model; calculation of unit-cell responsivity.

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