A Power-Free Mid-Infrared Photodetector with Tunable Selectivity

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Abstract

Graphene plasmons can resonantly enhance the incident light absorption and offer a potential for tunable spectral selectivity for mid-infrared (MIR) detection. High-performance tunable MIR plasmonic devices are, however, typically based on electrode-patterned graphene, which requires high power input and are technologically challenging in compact assembly. Here we demonstrate a tunable MIR photodetector array operating at zero input bias voltage. Our devices consist of integrating monolayer graphene with periodically “type-printed” ferroelectric superdomain. The spatial graphene carrier density patterns can be readily modulated by artificially defined ferroelectric superdomain with periodic nanoscale-wide stripe domains, achieving nonuniform patterning of conductivity and subsequently enabling graphene plasmons excitation and confinement for a selective transmission resonance in MIR regime. A high photoresponsivity of ~30 mA W⁻¹ at room temperature is achieved in our device. We also observe that our device array features a tunable detection performance from 7.2 to 8.5 μm by directly reconfiguring the periodicity of ferroelectric superdomain. Our strategy could lead to the development of smart fabrication of on-chip MIR photodetector array for applications of tunable spectral system with low-energy consumption.

Keywords: power-free detector; graphene plasmon; ferroelectric superdomain; tunable photodetector; mid-infrared detection
Mid-infrared (MIR) photodetector plays a vital role in biosensing, communication, thermal imaging, astronomy, spectroscopy, and security applications\textsuperscript{[1-6]}. In this frequency, graphene has attracted great interest for tunable and selective light detection because its intrinsic plasmons can be used to resonantly enhance absorption and externally controlled by applying gate voltage\textsuperscript{[1, 7-9]}. Exciting and tuning of plasmons in patterned graphene via traditional electrostatic gating have been demonstrated to be effective for MIR lights detection\textsuperscript{[5, 10-12]}. However, it has remained challenging to achieve high quality patterned graphene because of the inevitable edge-disorder and amorphization in graphene patterns defined by standard techniques\textsuperscript{[7, 13, 14]}, such as chemical vapour deposition (CVD) growth, lithographically, and ion/chemical etching. Recent efforts have been devoted to alternatively control graphene plasmons by chemical doping\textsuperscript{[15]} or patterned metal gratings\textsuperscript{[16, 17]}. The plasmonic devices using both above methods operate within single layer graphene (SLG) that do not require process of patterning graphene. For MIR light detection, precise modulation of graphene charge carrier with high concentration and nanoscale resolution is essential to efficiently excite plasmons and confine them to couple with incident lights, however, which has not yet extended. Additionally, these developed devices face common limitations in complex fabrication and require high power consumption\textsuperscript{[7, 9, 18]}.

Ferroelectric superdomain\textsuperscript{[19-21]}, offering nanoscale domains with alternately up-/down-ward polarization, provide possibility to spatially control graphene carrier density for nonuniform conductivity patterns construction, subsequently excite and confine graphene plasmons to resonantly enhance photoresponse. In this article, we artificially print a superdomain in BiFeO$_3$ (BFO) thin film with nanoscale-wide stripes to excite and confine graphene plasmons for tunable MIR detection. Carrier density spatially monitored by Raman signals suggest that ununiform patterning of graphene conductivity can be achieved by reconfiguring the ferroelectric superdomain. Tunable transmission spectra are detected for our devices without additional input power. Operating at zero-bias drain/source voltage and room temperature, a high photoresponsivity of $\sim$30 mA W$^{-1}$ at 8.5 $\mu$m is obtained. Importantly, we experimentally demonstrate that the device array do not require an external gate voltage and feature a tunable MIR detection performance by directly scaling the periodicity of ferroelectric superdomain.
Conceptual design and fabrication of device

Fig. 1a schematically illustrates the fabrication process and the structure of the photodetector designed in this work (see Methods for detail). Here we used a conductive atomic force microscope (AFM) probe (Bruker), with platinum-coating and tip radius ~30 nm, to construct ferroelectric superdomain, that is, the epitaxial ferroelectric BFO thin film was periodically switched to an adjacent upward and downward striped domain array (step 1). Of course, large-scale switching of ferroelectric superdomain has also been experimentally demonstrated in our previous work using water-printing technique\textsuperscript{[22]}. These above ferroelectric polarization switching combined with the advanced micro-/nano-lithography techniques can help achieve desired ferroelectric polarization patterns using large-scale type-printing method (ref. \textsuperscript{[22]}). Fig. 1b, c shows the crystal structure of BFO thin film using an annular bright-field (ABF) high-resolution scanning transmission electron microscopy (STEM). We can see iron atoms (yellow spheres) dramatically shift in upward or downward domains in the microscopy, respectively, indicating the direction of ferroelectric polarization had been reversed. The phase difference of adjacent domains is 180° (Fig. 1d), which is characterized by a piezoelectric force microscope (PFM). The period of polarized strips ($P$, sum of adjacent upward and downward domain width) was controlled from 10 μm to 200 nm in the same BFO film (Fig. S1). The upward domain width was kept equal with the downward domain in each period, that is, the width of ferroelectric domain stripes ($W$) ranges from 5 μm to 100 nm.

Then, we transferred a CVD-grown SLG sheet onto the BFO film (step 2) using wet transfer method\textsuperscript{[23]}. After this, to assess the graphene doping level induced by the electrostatic effect of remanent polarization in ferroelectric domains, we used a non-contact monitoring technique of Raman spectroscopy, where the Raman G-band frequency shifts can be used as a spatially resolved probe for the detection of graphene carrier-density\textsuperscript{[24]}. Fig. 1e maps the Raman G-band frequencies, revealing that the periodic stripes of the lower and higher frequencies directly relate to up-/down-polarized domains, respectively.

To facilitate photocurrent collection and reduce contact resistance, the source/drain electrodes were deposited on the graphene sheet (step 3). In general, the device presents a zero overall photocurrent if source/drain electrodes use a same metal. In this case, we employ an asymmetric metal-doped scheme to break that symmetric built-in electric field profile in the graphene channel, following the earlier report of metal-graphene-metal graphene operating at zero bias between source
and drain\[^2\]. In this case, we deposited 20-nm-thick palladium (Pd) and titanium (Ti) layers on graphene sheet, finally we covered an 80-nm-thick gold (Au) layer to prevent contact electrodes oxidation. A close-up scanning electron microscopy (SEM) image focusing on the active region of the as-fabricated device is given in Fig. 1f (also see an overall top-view optical microscope image for the device in Fig. S2). To exactly recognize the active region for fabrication and measurements, the BFO film was etched to a fixed rectangle region before polarization using the reactive ions etching method. The graphene sheet, highlighted with an orange color, shown in Fig. 1f (corresponding to the original SEM image in Fig. S3), covers only the fixed rectangle area and the excessive graphene was etched using oxygen plasma. The contact electrodes (white color) were deposited on the graphene sheet and the overlapped area is 1 \( \mu m \times 10 \mu m \).

Fig. 1. Architecture of graphene/BFO superdomain based photodetector.
(a) Schematic diagram of the experimental setup. The BFO film epitaxial growth on the STO substrate covered with LSMO electrode layer. The bright orange and dark wine stripes correspond the up- and down-polarized domains, respectively. The graphene was transferred on BFO film using improved wet method and the contact electrodes were deposited using sputter coating. Scanning transmission electron microscopy images of downward domain (b) and upward domain (c) in BFO thin film. The scale bars are 5 nm. (d) PFM phase images of switchable BFO domains. The scale bars of 90° and -90° indicate the periodical ribbons patterned adjacent upward and downward domains, respectively, and the period of poled domains (\( W \), sum of up- and down-polarized domain width). The upward domain width equals that of downward domain in each unit. (e) G-band frequency map for graphene on periodically poled BFO film with \( W = 1 \mu m \). Both scale bars in panels (d, e) are 1 \( \mu m \). (f) SEM image of the active area of the fabricated graphene/BFO device. The overlap length of contact electrode/graphene/BFO is 1 \( \mu m \). The fake color focuses on the graphene on BFO film.

Spatially controlling of graphene carrier density

Fig. 2a pictures the Raman G-band frequency of graphene on BFO with striped domains. Corresponding to period of 1000 nm in Raman mapping, the peak positions of Raman G-band for
graphene on upward and downward domains were 1586 and 1597 cm\(^{-1}\) (Fig. 2b), respectively. The periodic Raman frequency shifts from lower to higher range, indicating that the graphene owned a sharp transition from lower to higher carrier concentration at the edges of up- and down-polarized domains\[^{25,26}\]. For graphene, the formula of \[ \hbar \Delta \omega = \alpha' |E_F| \] (ref. \[^{24}\]) was used to estimate the doping level through the POG shifts (\(\hbar \Delta \omega\)) of graphene, where \(E_F\) is the Fermi energy and \(\alpha'\) is the integral constant (as given in Supplementary Section S1). The actual carrier concentration \((n)\) can be derived from the Fermi energy following \[ E_F = \hbar v_F \sqrt{\pi n} \] (ref. \[^{27}\]), where \(v_F = 1.1 \times 10^6\) m s\(^{-1}\) is the Fermi velocity. It suggested that the graphene carrier density on up- and down-polarized ferroelectric domains corresponds to \(\sim 3 \times 10^{12}\) cm\(^{-2}\) and \(\sim 1.2 \times 10^{13}\) cm\(^{-2}\), respectively. Due to the reversible and non-volatile merits for ferroelectric domain polarization and nanoscale resolution for ferroelectric domain size, it promisingly provides a novel approach for graphene carrier modulation as desired patterns. In principle, when the periodic doping of graphene matches to the incident wavelengths, this could enable graphene plasmonic resonance and enhance photocurrent of device in MIR range.

More quantitative information about the Raman G-band frequency is plotted in Fig. 2c. The average data were simultaneously collected during the process of Raman mapping measurements. The peak positions of G-band for graphene on upward and downward domains were around 1586 and 1597 cm\(^{-1}\), respectively. Free of tailoring graphene, we found that the POG shifts from lower frequencies to high frequencies to form a clear edge at the border of up- and down-polarized domain in all cases. The same phenomena can be also observed in other designed shapes. For example, we also observed that the Raman G-band frequencies shift by switching the upward domain as a circle pattern (Fig. S4). Due to the unshift of graphene G-band frequency on each striped up- or down-polarized domain, shown in Fig. 2a-c, it demonstrates that the spatial carrier patterns control over the reversible ferroelectric domain and the doping remains a stable level.

As above-mentioned, the graphene doping is estimated as \(\sim 3 \times 10^{12}\) cm\(^{-2}\) and \(\sim 1.2 \times 10^{13}\) cm\(^{-2}\) on up and down-polarized domains, respectively. The doping levels in graphene on up- and down-polarized domains are comparable to +121 meV (near the Dirac point) and −448 meV (typical \(p\)-doped), respectively, in conventional top-gated graphene transistor\[^{25}\]. The periodic patterns for graphene carrier modulation offer a novel approach to create multiple, parallel \(p-i\) junctions on graphene sheet without applied gate voltage or tailoring graphene. The schematic principle diagram
is shown in Fig. 2d. Iron atoms (yellow spheres) were dramatically deviated in upward or downward domains by applied voltage. This nonvolatile and recoverable feature provide key function of our device. This reversible feature in ferroelectric domains, easily switched using electric or large-area water printable technologies\(^{22, 28}\), range from micro- to nano-scales and thus provide a novel and feasible route to control graphene carrier density with a precise spatial resolution. Combined with the advances in switching ferroelectric domains, this proof of concept for rewritable graphene carrier patterns at nanoscale to create desired periodic arrays, such as micro- and nano-striped periodicities demonstrated here, could potentially be used to confine the intrinsic graphene surface plasmons for enhancing the photodetection in the infrared region.

Fig. 2. Doping graphene by type-printable ferroelectric superdomain. (a) AFM-Raman mapping images for graphene doped by periodically polarized ferroelectric domains. The period of ferroelectric domain ranges from 1 μm to 200 nm, where stripe width of the up- and down-polarized domains is the same in each sample. All the scale bars are 1 μm. (b) Averaged Raman frequencies for graphene on upward (orange spheres) and downward (wine spheres) domains and peak positions are \(\sim 1586 \text{ cm}^{-1}\) and \(\sim 1597 \text{ cm}^{-1}\), respectively. The solid lines are the Lorentz fitting results. (c) Position of graphene G-band peaks as function of representative domain period. The Raman G-band frequency averages over a down-polarized domain (wine crosses) and an up-polarized domain (orange crosses). Error bars indicate the S.D. of the Raman G-band frequencies shift and domain periods in each stripe. (d) Schematic of the device focusing on the graphene/BFO interface. The graphene on down-polarized and up-polarized domains follows p-doped and near-intrinsic graphene behaviors, respectively.
Tuning of graphene plasmons by ferroelectric superdomain

Then we focus on the optical performance of graphene on various patterned BFO ferroelectric domains. We employ an AFM probe to guide the incident light to specific micro regions, as schematically illustrated in Fig. 3a. The schematic of this transmission measurement is shown in the inset of Fig. 3b, where \( T \) and \( T_0 \) represent the transmission of BFO film epitaxial growth on STO substrate with and without graphene, respectively. The transmission extinction in this architecture, \( 1 - T/T_0 \), can be expressed by following equation (1) (ref. \([12]\)):

\[
1 - \frac{T}{T_0} = 1 - \frac{1}{|1 + Z_0 \sigma(\omega) / (1 + n_s)|^2}
\]

which is directly related to the dynamical conductivity \( \sigma(\omega) \) of graphene; \( Z_0 \), \( \omega \), and \( n_s \) represent the vacuum impedance, the frequency of the light, and the refractive index substrate, respectively.

The measured extinction spectra of the graphene/BFO hybrid structures are presented in Fig. 3b. The gray squares, orange diamonds, and wine triangles present the measured \( 1 - T/T_0 \) of graphene on pristine BFO film (unpolarized), single ferroelectric domain with upward and downward polarization, respectively. The solid lines correspond to the fitted results following equation (1), and the dynamical conductivity of graphene is fitted using Drude model\([27]\). Detailed dynamical conductivity fitting procedures are shown in Supplementary Section S2. The doping of graphene in such cases is estimated by the Raman G-band frequency shift (Figs. S5, S6). The graphene carrier concentration is between \( \sim 2 \times 10^{12} \) cm\(^{-2} \) and \( \sim 3 \times 10^{12} \) cm\(^{-2} \) both on pristine and single upward domain BFO, and increases to \( \sim 1.1 \times 10^{13} \) cm\(^{-2} \) on single downward domain, further verifying the observations of the Raman frequencies shift for graphene on periodically poled BFO (Fig. 1e and Fig. 2b). Notably, the contribution of graphene on single downward domain to the transmission extinction can be ignored, and the contribution of graphene on single upward domain and pristine BFO as well.

The extinction spectra \( (1 - T/T_0) \) for graphene on periodically poled BFO with domain period \( (P) \) ranging from 10 \( \mu \)m to 200 nm are shown in Fig. 3c, d. In these cases, the length \( (L) \) and width \( (W) \) both upward and downward) of striped ferroelectric domain are 10 \( \mu \)m and \( P/2 \), respectively. We observe three prominent features in these periodically doping graphene stripes. Firstly, the extinction intensity increases significantly when \( P \) is below 1 \( \mu \)m. Secondly, it occurs a remarkably selective resonant peak with \( P \) from 1 \( \mu \)m to 200 nm. Thirdly, the resonant peaks shift from low frequency (1184 cm\(^{-1} \)) to high frequency (1392 cm\(^{-1} \)) with decreasing domain period. According to the Raman
G-band frequencies (Fig. 2b), we fit the spectra with solid lines employing the graphene at the same doping level in each patterned carrier, that is $3 \times 10^{12}$ cm$^{-2}$ and $1.2 \times 10^{13}$ cm$^{-2}$ on upward and downward domains, respectively. The detail fitting procedures are presented in Supplementary Section S2, according to equation (1).

To realize the enhanced transmission extinction and the frequency selectivity beyond broadband wavelengths response, we introduce a plasmonic resonance model in a graphene/ferroelectric hybrid structure without lithographically patterning graphene onto BFO film arranged in a periodically polarized domains array, as shown in Fig. 3a. The spatial carriers in graphene driven by ferroelectric polarization and modulated by applying voltage have been reported$^{[26, 29]}$. However, few investigations focus on directly tuning the graphene plasmons using rewritable ferroelectric domains at subwavelength scale without gating voltage. In this work, we preliminarily investigate the coupling effect of graphene plasmons and incident wavelengths using finite element method. Fig. 3e shows the simulated cross-section of electric field of our device and the detailed simulating procedures are presented in Supplementary Section S3. For example, when the domain period ($P = 1$ μm) matched to the incident wavelength (8.45 μm), the highly confined graphene plasmons are resonant to the incident photons, resulting in a remarkable enhancement of local electric field in graphene at the edges between up- and down-polarized domains. The corresponding $x$- and $y$-component of the surface electric field are shown in Fig. 3f and Fig. 3g, respectively. In this case, we set the chemical potential ($\mu_c = E_F$) of graphene doping by upward and downward domains ($P = 1$ μm) as +121 meV and −448 meV (estimated from Fig. 2b), respectively. The energy of the transverse-magnetic (TM) mode is strongly confined at the graphene/ferroelectric interface (Fig. 3f and Fig. 3g, corresponding to Fig. 3e) with ultra-high enhanced electric field intensity. Although the energy flow gets into the graphene structure on the up-polarized ferroelectric domain, it is almost perfectly absorbed. This phenomenon might be related to the electronic behavior near the upward and downward ferroelectric doping graphene junctions.
Fig. 3. Tunable graphene photoresponse modulated by ferroelectric superdomain. (a) Schematic of nano-infrared spectra setup. The concentric light-blue circles represent propagating plasmonic waves launched by the tip and reflected by the graphene. The red wave lines indicate the directions of the graphene plasmon transformation. The domain width $W$ (upward or downward) equals a half of a ferroelectric domain period $P$. (b) Extinction in transmission, $1-T/T_0$, for graphene on pristine BFO (unpoled, gray squares), BFO with single up-polarized domain (orange diamonds) and single down-polarized domain (wine triangles). Solid lines are corresponding fitting results. The inset is a schematic of the measurement. $T_0$ and $T$ represent the transmittance of bare epitaxial growth BFO substrate and graphene/BFO structure, respectively. (c, d) Transmission extinction for graphene on periodically poled BFO film with domain period from 10 $\mu$m to 200 nm. It reveals that the structures possess a remarkably enhancing and selective transmission in the mid-infrared region when the carrier strips are under nanoscale resolution. (e) Simulated surface electric field (cross-section view) of graphene/BFO hybrid structure with periodically polarized ferroelectric domains. Corresponding $x$- (f) and $y$- (g) component of the surface electric field in panel (e). The simulated results confirmed the periodically polarized ferroelectric stripes can effectively confine graphene plasmons, yielding the coupling effect of graphene plasmons and incident wavelengths.
**Tunable mid-infrared detection performance**

To measure the photocurrent of our device, the incident signals generated by an automated wavelength tuning laser resource were added on the SLG sheet at 90° (in vertical direction) with a zero-bias voltage on source/drain ($V_{SD}$). Due to rewritable merits for controlling graphene carrier patterns, it gives a feasible method to modulate the photodetection by varying the ferroelectric domain period. The fabricated devices are presented in Fig. 4a and Supplementary Fig. S2. We first study the photocurrent information in the graphene/ferroelectric structures, as mapping in Fig. 4b. All these photocurrents are obtained at the peak values by 12 points under each wavelength illumination. The highest photocurrents in each unit are therefore achieved near the resonant wavelengths when the domain periods are below 1 μm. In contrast, when we increase the size of the periodic domain from 1 μm to 5 μm or 10 μm, the selectivity of photoresponse in our device is yet shown in Fig. 4b, ranging from 8.8 to 6.6 μm due to the surface plasmons mismatched to the graphene carrier-density array. Thus, it is concluded that the contribution for enhancing photocurrent can be ignored when the domain period exceeds 5 μm ($P=5, 10 \mu m$), and the behavior is more likely as the single downward polarized ferroelectric domain doped graphene.

We further investigate the photoresponsivity, $R_{ph} = I_{ph}/P_{in}$, where $I_{ph}$ and $P_{in}$ are the photocurrent and incident laser power, respectively[10]. The plots in Fig. 4c show the peak photoresponsivity (29.73 mA W$^{-1}$) of our device with domain period of 1 μm is much higher (~24 folds) than that of a single downward polarized domain (1.23 mA W$^{-1}$). All the photoresponsivity data of our devices are summarized in Fig. 4d. It shows that our devices present a remarkable tunability and selectivity for detection light with different wavelengths. Moreover, the photoresponsivity of devices remains remarkably high values in the region from 8.5 to 7.2 μm and possesses an ultra-high enhanced factor $\beta$, the ratio of the highest $R_{ph}$ between devices with $P$ ranging from 5 μm to 200 nm and the device of graphene on BFO with single downward domain, on the order of 8.5~24 (Fig. 4b) with different period of graphene carrier patterns. These highly tunable properties of mid-infrared light detection could be attributed to the strong graphene plasmons excited by periodically striped ferroelectric domain array.
Fig. 4. Detection performances of graphene/ferroelectric superdomain device. (a) Integrating graphene photodetectors array on BFO film. The top column is the optical image of fabricated devices array, which consists of graphene on periodically polarized ferroelectric domains and source/drain (S/D) electrodes. The bottom column lists the PFM phase images for periodically polarized BFO domains with different size, which corresponds to the devices shown in top column. (b) Tunable photoresponse as a function of incident wavelength and BFO domain period. Photocurrent mapping: incident wavelength dependent photocurrent for these graphene/BFO devices with different ferroelectric domain periods. The scale bar is plotted on a linear color. The currents of the device were measured under zero source–drain bias voltage. The laser wavelengths are modulated from 8.8 to 6.6 μm with a spot size of 5 mm, covering the entire device. The peak photoresponsivity ($R_{ph}$) enhancement factor curves are displaced by 23 units. (c) Photoresponsivity comparison of photodetectors based on graphene doped with different period for switching domain strips. The highest $R_{ph}$ of photodetector with domain period $P = 1$ μm is enhanced by 24 folds to that of device with $P = 10$ μm. (d) Photoresponsivity vs. incident wavelengths for photodetector with rewritable graphene carrier stripes. The highest photoresponsivity of as-prepared devices in mid-infrared region is up to ~30 mA W$^{-1}$.

We now turn to the performance of the typical graphene MIR photodetectors, and the key merits are listed in Table 1. Compared with the earlier reported metal plasmon-enhanced graphene MIR
photodetectors, e.g. metal-graphene-graphene\(^2\), the intrinsic plasmon in patterned graphene offers an incomparable advantage in the mid-infrared range: its surface plasmons could be used to resonantly enhance absorption\(^5\) for tunable photodetection controlled with a grating effect, providing an appealing spectral selectivity with ultra-high tunability\(^10\). For our photodetector demonstrated here, it harvests an ultra-high enhanced photoresponsivity up to \(\sim 30 \text{ mA W}^{-1}\) under 8.5 \(\mu\text{m}\) illumination. The obtained photoresponsivity is not highest to record in graphene photodetectors, but is comparable to that of conventional graphene plasmonic device for MIR detection based on nanopatterned photograting structures. This ultra-high responsivity could attribute to the effective plasmon excitations and perfect crystallinity in graphene sheet, and the latter can effectively reduce the light scattering compared with the nanopatterned graphene. Moreover, with the conveniently writing of graphene carrier-density patterns by switching ferroelectric domains at nanoscale, avoiding the complex nanofabrication in conventional graphene plasmonic devices, the fabricated device owns a remarkably selective response over broadband wavelengths in the mid-infrared region.

### Table 1. Performance parameters of graphene-based MIR photodetectors

| Type                                                                 | Photoresponsivity | Detection Range | Tunable spectral selectivity | Enhancement factor | Ref.                        |
|---------------------------------------------------------------------|-------------------|-----------------|-----------------------------|-------------------|-----------------------------|
| Graphene plasmon / ferroelectric superdomain                       | \(\sim 30 \text{ mA W}^{-1}\) | 8.5–7.2 \(\mu\text{m}\) | Yes                         | 24X               | This work                   |
| Metal array-graphene-metal array                                   | 6.1 \(\text{mA W}^{-1}\) | 300 nm–6 \(\mu\text{m}\) |                             |                   | Mueller T., et al. \(^2\)  |
| Graphene nanoribbon array                                          | 0.008 \(\text{mA W}^{-1}\) | 10.6 \(\mu\text{m}\)   | Yes                         | 15X               | Freitag M., et al. \(^10\) |
| Graphene-disks connected by graphene nanoribbons                  | 16 \(\text{mA W}^{-1}\) | 12.2 \(\mu\text{m}\)   | Yes                         |                   | Guo Q., et al. \(^5\)      |
Conclusions

We have fabricated a power-free MIR photodetector consisting of integrating monolayer graphene with BFO thin film with nanoscale-wide stripe superdomain. Raman shifts are detected for non-contact monitoring dopants in graphene. We observe nanoscale doping patterns on ferroelectric superdomain, and charge carrier density is estimated to reach $1.3 \times 10^{13} \text{ cm}^{-2}$. The devices work at zero-bias drain/source voltage and exhibit an enhanced photoresponsivity of $\sim 30 \text{ mA W}^{-1}$ at room temperature due to the resonant coupling graphene plasmons with incident lights. Furthermore, the device owns a selective response over broadband from 7.2 to 8.5 μm by directly reconfiguring the ferroelectric domain period under ambient condition, which is free of applying external gate voltage. The precisely spatial controlling graphene carrier-density by reversing ferroelectric domain with nanoscale demonstrated in this work, as the excellent compatibility of graphene sheets radically integrating to different substrates, shows many attractive advantages than those conventional devices using complex nanofabrication. Moreover, the recent development of graphene synthesis and transfer techniques for high-quality graphene obtained, as well the green and large-scale printing technologies for switching ferroelectric domains with nanoscale resolution, pave the way for the future integrated optoelectronics platform.

Methods

**BFO film epitaxial growth.** BFO thin films were epitaxial grown on (001)-oriented STO substrates with LSMO as the bottom electrode using a pulsed laser deposition method. For deposition of both LSMO and BFO films, a KrF excimer laser, with 248 nm wavelength, 5 Hz repetition rate and $\sim 1.5 \text{ J cm}^{-2}$ energy density, was employed. The films were grown in an atmosphere of 0.2 mbar oxygen pressure at 700 °C. The thickness of the films was controlled at $\sim 25 \text{ nm}$.

**Device fabrication.** For ferroelectric polarization switching, the up-polarized (down-polarized) domains were switched by scanning the surface with a nanotip under $+12 \text{ V} (-12 \text{ V})$ bias exceeding the coercive voltage (Fig. 1a, step 1). For the convenience of guiding incident light to the specific areas and fixing the active illuminating regions, the BFO film was patterned to an array with a fixed area in each unit using a reactive ion etching (RIE) method before polarization. The etched depth was controlled at $\sim 10 \text{ nm}$ by ion reactive time.

The single-layer graphene was transferred on BFO film using an improved wet method (Fig. 1a, step 2). Briefly, the polymethyl methacrylate (PMMA, Aladdin) solution (20 mg mL$^{-1}$) was spin-
coated on CVD-grown monolayer graphene/copper foils (SixCarbon Technology Shenzhen) at 3000 rpm for 30 s and dried at 120 °C for 90 s in air. Ammonium persulfate (0.1 M, Aladdin) was used to etch copper substrate, and the PMMA/graphene film was washed by deionized water several times to remove the etchant residue. Then the pre-polarized BFO film was placed in water with a tilting angle underneath the PMMA/graphene film to support it. After drying in air, the PMMA was removed with an acetone bath at 50 °C and washed with ethanol. The monolayer graphene was also etched to the same area as the marked BFO using oxygen plasmon. Subsequently, the source and drain electrodes of Au/Ti and Au/Ni were deposited on the border of graphene to completely fabricate the device (Fig. 1a, step 3). The thicknesses of Au layer and both Ti and Pd layers are 80 and 20 nm, respectively.

**Measurements.** PFM experiments were performed in ambient conditions at room temperature with an Infinity Asylum Research AFM. The crystal structures of the BFO were performed using TEM (JEOL 2100F) operated at 200 keV and equipped with probe aberration corrector (CEOS) and double spherical aberration (Cs) correctors. The spatial resolution of the microscope can reach 90 pm at the incident semi-angle of 20 mrad. Then fast-Fourier-transform multi-slice approach was used for the STEM configuration. Raman-AFM mapping images and corresponding spectral data in the same region were acquired on a fully integrated system based on Smart SPM state of the art scanning probe microscope and XploRA Raman micro-spectrometer (HORIBA). In all cases, 532 nm laser excitation and tip-enhanced Raman spectroscopic resolution were used. The transmission spectra were collected using a Spotlight 200i FT-IR Microscopy System (PerkinElmer Inc.) with spot resolution better than 10 μm. The photocurrents were performed using a Keithley 4200A-SCS Parameter Analyzer (Tektronix), and the incident source was produced by a tunable laser (EKSPLA, 2.3–10 μm), at zero bias voltage between the source and drain electrodes. The laser intensities, including Raman and electrical measurements, were set below 1 mW to avoid the artefacts caused by the laser-induced heating. All measurements were performed in ambient air at room temperature.

**Numerical calculation.** The electrical properties of graphene were calculated using the random-phase approximation (RPA), and the dynamic optical response of graphene can be derived from the Kubo formula (Supplementary Section S2) (ref. [30, 31]). The electromagnetic field simulation was performed using finite element methods (Supplementary Section S3).
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Author contributions
J.G., W.H. and J.Z. conceived and designed the experiments. Y.T., Y.Z. and J.Z. provided the epaxial growth BFO films. Y.T. and Y.Z. wrote the ferroelectric superdomain with type-printing technique and characterized the PFM images. J.G., Y.L., S.L. and L.L. fabricated the devices. Q.Z. and L.G. conducted the high-resolution TEM characterization. S.L. and L.L. conducted the SEM characterization. J.G., T.G. and W.H. conducted the Raman characterization and optical transmission measurements. J.G. and S.L. conducted the photodetection experiments. J.G., J.C., Y.L., J.Y. and L.L. performed the thermotical models and calculations. J.G., Yuan. L., X.Z., W.H. and J.Z. analysed the data. W.H. and J.Z. supervised the experimental study. J.G. and Y.L. wrote the paper and the Supporting Information.

Competing interests
The authors declare no competing interests.

Data availability
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Additional information
Supporting Information
Supplementary Section S1-S3 and Figs. S1-S6.

References
[1] D. Rodrigo, O. Limaj, D. Janner, D. Etezadi, F. Javier Garcia de Abajo, V. Pruneri, H. Altug, Science 2015, 349, 165.
[2] T. Mueller, F. Xia, P. Avouris, Nat. Photonics 2010, 4, 297.
[3] M. Yu, Y. Okawachi, A. G. Griffith, N. Picque, M. Lipson, A. L. Gaeta, Nat. Commun. 2018, 9, 1869.
[4] A. Tittl, A. Leitis, M. Liu, F. Yesilkoy, D.-Y. Choi, D. N. Neshev, Y. S. Kivshar, H. Altug, Science 2018, 360, 1105.
[5] Q. Guo, R. Yu, C. Li, S. Yuan, B. Deng, F. J. Garcia de Abajo, F. Xia, Nat. Mater. 2018, 17, 986.
[6] J. A. Sinclair, G. S. Orton, J. Fernandes, Y. Kasaba, T. M. Sato, T. Fujiyoshi, C. Tao, M. F. Vogt, D. Grodent, B. Bonfond, J. I. Moses, T. K. Greathouse, W. Dunn, R. S. Giles, F. Tabataba-Vakili, L. N. Fletcher, P. G. J. Irwin,
[7] T. Low, P. Avouris, *ACS Nano* **2014**, 8, 1086.

[8] G. X. Ni, L. Wang, M. D. Goldflam, M. Wagner, Z. Fei, A. S. McLeod, M. K. Liu, F. Keilmann, B. Ozyilmaz, A. H. C. Neto, J. Hone, M. M. Fogler, D. N. Basov, *Nat. Photonics* **2016**, 10, 244.

[9] F. H. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, *Nat. Nanotechnol.* **2014**, 9, 780.

[10] M. Freitag, T. Low, W. Zhu, H. Yan, F. Xia, P. Avouris, *Nat. Commun.* **2013**, 4, 1951.

[11] H. Yan, T. Low, W. Zhu, Y. Wu, M. Freitag, X. Li, F. Guinea, P. Avouris, F. Xia, *Nat. Photonics* **2013**, 7, 394.

[12] H. Yan, X. Li, B. Chandra, G. Tulevski, Y. Wu, M. Freitag, W. Zhu, P. Avouris, F. Xia, *Nat. Nanotechnol.* **2012**, 7, 330.

[13] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192.

[14] A. C. Ferrari, F. Bonaccorso, V. Fal'ko, K. S. Novoselov, S. Roche, P. Bøggild, S. Borini, F. H. Koppens, V. Palermo, N. Pugno, *Nanoscale* **2015**, 7, 4598.

[15] F. S. Hage, T. P. Hardcastle, M. N. Gjerding, D. M. Kepaptsoglou, C. R. Seabourne, K. T. Winther, R. Zan, J. A. Amani, H. C. Hofsæs, U. Bangert, K. S. Thygesen, Q. M. Ramasse, *ACS Nano* **2018**, 12, 1837.

[16] T. J. Echtermeyer, S. Milana, U. Sassi, A. Eiden, M. Wu, E. Lidorikis, A. C. Ferrari, *Nano Lett.* **2016**, 16, 8.

[17] D. Wang, A. E. L. Allcca, T. F. Chung, A. V. Kildishev, Y. P. Chen, A. Boltasseva, V. M. Shalaev, *Light-Sci. Appl.* **2020**, 9, 126.

[18] M. Long, P. Wang, H. Fang, W. Hu, *Adv. Funct. Mater.* **2019**, 29, 1803807.

[19] N. A. Spaldin, R. Ramesh, *Nat. Mater.* **2019**, 18, 203.

[20] S. H. Baek, H. W. Jang, C. M. Folkman, Y. L. Li, B. Winchester, J. X. Zhang, Q. He, Y. H. Chu, C. T. Nelson, M. S. Rzchowski, X. Q. Fan, R. Ramesh, L. Q. Chen, C. B. Eom, *Nat. Mater.* **2010**, 9, 309.

[21] E. Langenberg, H. Paik, E. H. Smith, H. P. Nair, I. Hanke, S. Ganschow, G. Catalan, N. Domingo, D. G. Schlom, *ACS Appl. Mater. Inter.* **2020**, 12, 20691.

[22] Y. Tian, L. Wei, Q. Zhang, H. Huang, Y. Zhang, H. Zhou, F. Ma, L. Gu, S. Meng, L.-Q. Chen, C.-W. Nan, J. Zhang, *Nat. Commun.* **2018**, 9, 3809.

[23] J. W. Suk, A. Kitt, C. W. Magnuson, Y. Hao, S. Ahmed, J. An, A. K. Swan, B. B. Goldberg, R. S. Ruoff, *ACS Nano* **2011**, 5, 6916.

[24] S. Pisana, M. Lazzeri, C. Casiraghi, K. S. Novoselov, A. K. Geim, A. C. Ferrari, F. Mauri, *Nat. Mater.* **2007**, 6, 198.

[25] A. Das, S. Pisana, B. Chakraborty, S. Piscanec, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari, A. K. Sood, *Nat. Nanotechnol.* **2008**, 3, 210.

[26] C. Baeumer, D. Saldana-Greco, J. M. Martinez, A. M. Rappe, M. Shim, L. W. Martin, *Nat. Commun.* **2015**, 6, 6136.

[27] Q. Bao, K. P. Loh, *ACS Nano* **2012**, 6, 3677.

[28] Y.-H. Chu, Q. He, C.-H. Yang, P. Yu, L. W. Martin, P. Shafer, R. Ramesh, *Nano Lett.* **2009**, 9, 1726.

[29] C. Baeumer, S. P. Rogers, R. Xu, L. W. Martin, M. Shim, *Nano Lett.* **2013**, 13, 1693.

[30] E. Hwang, S. Adam, S. D. Sarma, *Phys. Rev. Lett.* **2007**, 98, 186806.

[31] T. Stauber, *J. Phys.-Condens. Mat.* **2014**, 26, 123201.