Graphene-based photodetectors have demonstrated mechanical flexibility, large operating bandwidth, and broadband spectral response. However, their linear dynamic range (LDR) is limited by graphene’s intrinsic hot-carrier dynamics, which causes deviation from a linear photoreponse at low incident powers. At the same time, multiplication of hot carriers causes the photoactive region to be smeared over distances of a few micrometers, limiting the use of graphene in high-resolution applications. We present a novel method for engineering photoactive junctions in FeCl₃-intercalated graphene using laser irradiation. Photocurrent measured at these planar junctions shows an extraordinary linear response with an LDR value at least 4500 times larger than that of other graphene devices (44 dB) while maintaining high stability against environmental contamination without the need for encapsulation. The observed photoresponse is purely photovoltaic, demonstrating complete quenching of hot-carrier effects. These results pave the way toward the design of ultrathin photodetectors with unprecedented LDR for high-definition imaging and sensing.

**INTRODUCTION**

Intense research activity on graphene-based photodetectors (1) has demonstrated a unique range of properties, including mechanical flexibility (2), large operating bandwidth (3), and broadband spectral response. However, state-of-the-art inorganic (Si, Ga, GaAs, etc.) photodetectors currently exhibit a linear response over a larger range of optical powers, as compared to graphene. This is due to the comparatively small density of states in graphene at energies below 1 eV. Furthermore, the thermal diffusion of photogenerated carriers has been found to dominate photocurrent signals measured by graphene-based photodetectors (4–6). These strong photothermoelectric (PTE) effects enable multiplication of hot carriers but also cause photoresponsive regions to be smeared out over distances exceeding 2 μm (5–7). The narrow linear dynamic range (LDR) and the size of the photoresponsive regions in graphene photodetectors limit integration of graphene pixels in high-resolution sensing and video imaging applications.

Chemical functionalization (8) is a largely unexplored route to overcoming the intrinsic limitations on sensing introduced by hot-carrier dynamics in pristine graphene, where the limited size of the Fermi surface imposes tight constraints to the carrier relaxation dynamics (9). Although attempts have been made to use chemical functionalization to engineer p-n junctions in graphene (10, 11) and selectively define photoresponsive regions (2, 12, 13), no major improvements have been shown compared to pristine graphene devices; therefore, several challenges remain. These include finding forms of functionalization that give ultrahigh values of charge doping and are also air-stable. Functionalization of graphene with FeCl₃ has been found to result in record-high levels of hole-doping (≈ 1 × 10¹⁵ cm⁻²) with a room temperature electrical conductivity up to 1000 times larger than that of pristine graphene while maintaining equivalent absorption over the visible wavelength range (14, 15). At the same time, an unforeseen stability under harsh environmental conditions (16), the ease of large-area processing (15), and the promise for efficient coupling of telecommunication wavelength light to electrical signals through surface plasmons make this material uniquely suited for exploring novel optoelectronic applications. The development of a new generation of imaging arrays with unprecedented LDR and pixel density, which do not use any thermal isolation or electrostatic gating at high voltages and are stable under both ambient and harsh conditions, would bring imaging and sensing technologies to new frontiers.

Here, we demonstrate micrometer- and nanometer-scale planar photoresponsive junctions, which are directly written in the host material using focused laser light. Characterization of photocurrent signals reveals a purely photovoltaic (PV) response and an LDR as large as 44 dB, which is at least 4500 times larger than that of any previously reported graphene photodetector (3, 9, 17–20). Crucially, these detectors exhibit marked stability under atmospheric conditions without any form of encapsulation and maintain a broad spectral response from ultraviolet A (UVA) to midinfrared (MIR) wavelengths. Using emerging nanophotonics tools, such as near-field photocurrent nanoscopy, we can surpass the diffraction-limited resolution of far-field methods and define photoresponsive junctions smaller than half the laser wavelength used.

The light-assisted design of integrated and atomically thin optoelectronic circuits is a step forward to a new frontier in high-definition sensing applications, whereas FeCl₃-intercalated few-layer graphene (FeCl₃-FLG) defines a new paradigm in ultrathin, high-LDR photodetectors.

**RESULTS AND DISCUSSION**

**Preparation of laser-defined junctions**

The starting material to achieve our goal is an intercalated four-layer graphene flake with FeCl₃ introduced only between the top three carbon layers. Intercalation of FeCl₃ molecules into mechanically exfoliated FLG on a Si/SiO₂ substrate was conducted using a previously reported method (14) in a two-zone furnace (see Materials and Methods). A typical Raman spectrum of this system shows the G₀ peak at 1580 cm⁻¹ due to the E₂g phonon mode of pristine graphene as well as the blue-shifted G₁ = 1615 cm⁻¹ and G₂ = 1625 cm⁻¹ peaks of the same mode caused by the charge doping of FeCl₃ molecules adjacent to only one side of a graphene layer (stage 2) or sandwiching the carbon atoms (stage 1) (see Fig. 1A). Upon its exposure to 532-nm laser light with an incident power of...
15.3 MW/cm² for 3 s, we observe drastic modifications in the Raman G band: a pronounced downshift of the G peak positions; a reduction of their full width at half maximum; the disappearance of the G₂ peak; and the emergence of the G₀ peak (see Fig. 1A). All these changes indicate a reduction in hole doping caused by laser-induced displacement of FeCl₃, with the disappearance of the G₂ peak stemming from the complete removal of stage 1 intercalation. Finally, the absence of a defect-related Raman peak demonstrates that this functionalization can truly sustain laser powers more than 300 times higher than those of pristine graphene (section S1).

To ascertain the effectiveness of laser irradiation as a method for locally tailoring FeCl₃ intercalation in graphene, we exposed a 5.5-μm-wide section of the intercalated flake to a raster laser scan (15.3 MW/cm² for 3 s in 0.5-μm steps). Raman spectra were collected at incrementally spaced locations across the laser-exposed region both before and after illumination, as shown in Fig. 1B. Comparing the spectral profiles at each location, it is apparent that all irradiated regions undergo a substantial degree of deintercalation. In Fig. 1C, we quantify changes in chemical structure across the entire laser-exposed region by analyzing the positions of the G₁ and G₂ peaks along a 21-μm line scan. Uniform removal of the G₂ peak from the entire rastered region demonstrates that FeCl₃ molecules may be displaced from arbitrarily mapped areas. The degree of intercalation remains unchanged away from the irradiated area, with the resolution of FeCl₃ displacement defined by the laser spot profile. The marked effectiveness of laser-induced deintercalation over a significant fraction of the FeCl₃-FLG flake area presents an elegant method, akin to optical lithography, which can be used to locally customize the chemical functionalization of graphene layers.

The shift of the Raman G peak is quantitatively translated into a charge density using the model developed by Lazzeri et al. (21) and Das et al. (22) with an accuracy of ±10%, as shown by independent characterization of charge density from quantum oscillations in magnetoresistance (14, 15). We find that the laser irradiation of FeCl₃ causes a reduction in charge density of up to Δρₕₒₜ ≈ −0.6 × 10¹⁴ cm⁻² (Fig. 2A), which agrees with electrical measurements showing a 170% increase in resistivity over the modified area (see section S4). Hence, the abrupt change in hole concentration at the boundaries of the laser-exposed region defines sharp p-p’ junctions (see section S2.5 for data on additional devices).

Optoelectronic response of laser-defined p-p’ junctions
Inspired by the rich variety of charge transfer processes, which has enabled a revolution in semiconductor heterostructure applications, we examined the optoelectronic response of these laser-defined junctions in FeCl₃-FLG. Laser light focused to a beam spot diameter of 1.0 μm at 300 mW was rastered over the device surface while measuring...
incident photons generate a density (FeCl₃ (white dashed lines). The photoresponse is measured for excitation wavelengths of 375, 473, and 561 nm.

The observed difference originates from the charge carrier dynamics. More specifically, in pristine graphene, the chemical potential (μ) lies close to the charge neutrality point, and the small Fermi surface imposes tight constraints on the maximum energy lost through momentum-conserving acoustic phonon emission (ΔE_ac < 2hv_k, where v_k ~ 2 × 10⁴ ms⁻¹ is the acoustic phonon speed and k is the hot carrier wave number) (23). As a result, photoexcited carriers reach a steady-state temperature far above that of the lattice (T_h >> T_l) and are instead cooled via short-range “supercollision” processes at sites of disorder (9, 24). If the PTE effect is similarly responsible for photocurrent in FeCl₃-FLG, the steady-state temperature of hot carriers must lie significantly closer to that of the lattice (T_h ~ T_l << T_l) to justify the observed linear power dependence (9). A reduction in T_h can be explained by the ultrahigh levels of charge density (up to 3 × 10¹⁴ cm⁻² per layer) achieved through FeCl₃ intercalation (14); the expanded Fermi surface enhances ΔE_ac to as much as 60 times that of pristine graphene, accelerating the cooling of photogenerated charges. On the other hand, the small temperature gradients present at these highly doped junctions could diminish thermoelectric currents so much that they become negligible compared to signals generated by the PV effect. A linear power dependence would also be expected in this case (25), provided that the incident light intensity is sufficiently low so as to not affect the average lifetime (τ) of photogenerated carriers. The observation of photocurrent with a linear dependence on incident power therefore indicates enhanced cooling of hot carriers in FeCl₃-FLG but, as other studies have suggested (19), cannot be used independently to distinguish between PTE and PV effects.

**Photovoltaic effect in FeCl₃-FLG junctions**

To identify the origin of photocurrent at p-p' junctions of FeCl₃-FLG, we adapt the model of Song et al. (5) to calculate the relative contributions of the PTE and PV effects (section S5). The photocurrent produced in a p-p' junction located in the middle of an FeCl₃-FLG...
channel (length \( L \) and width \( W \)) illuminated by a laser (spot diameter \( l_0 \)) is

\[
I_{ph} = \int_0^W \int_{-l/2}^{l/2} \left[ S_{(x,y)} \nabla T_{(x,y)} - \sigma_{\text{ph}}^{-1}(x,y) \nabla \mu_{\text{ph}}(x,y) \right] dy dx \frac{R}{W} \tag{1}
\]

where \( R \) is the resistance of the graphene layer and \( \eta \) is the carrier mobility. For a doped graphene layer with a charge carrier density above \( n \approx 3 \times 10^{11} \text{ cm}^{-2} \), the Bloch-Grüneisen temperature \( T_{BG} = \Delta E_0/k_B \) exceeds 300 K (26). Therefore, under continuous wave illumination, where \( \Delta T \) is typically just a few kelvin (7), bottlenecks in electronic-acoustic phonon coupling are alleviated in FeCl\(_3\)-FLG. The increased efficiency of momentum-conserving acoustic phonon emission renders supercollisions irrelevant to hot-carrier cooling processes and reduces the average cooling length \( \zeta \) from several micrometers (5, 7) to approximately 200 nm. Hence, for a typical device, \( \zeta < L/2 \). Using the low-energy-density states for monolayer graphene and a minimum conductivity of \( \sigma_{\text{min}} \approx 4e^2/h \) (27), we express the conductivity of each decoupled layer as a function of its chemical potential \( \sigma(\mu) = \sigma_{\text{min}}(1 + \mu^2/\Lambda^2) \), where \( \Lambda \approx 140 \text{ meV} \). The Mott relation for thermopower (27) and a solution to the heat equation, which assumes nondivergent current densities, (5) are then used with Eq. 1 to estimate the relative magnitudes of PTE and PV currents from the electrical properties on either side of the p-p’ junction

\[
\frac{I_{PTE}}{I_{PV}} = \frac{2e k_B T_h l_0 \sigma_{\text{min}}}{\mu' \eta' \tau' \Lambda} \left[ \left( \frac{1 - \frac{\sigma_{\text{min}}}{\sigma'} \right) - \frac{1 - \frac{\sigma_{\text{min}}}{\sigma''}}{\tau' + \tau''} \right] \left( \tan^{-1}(\frac{\sigma'}{\tau'}) - \tan^{-1}(\frac{\sigma''}{\tau''}) \right) \right] \tag{2}
\]

with 1 ps < \( \tau < 2 \) ps, which is in agreement with pump-probe spectroscopy measurements (28) (see section S5), and all material parameters are averaged over the device width. For each of the decoupled monolayers in the four-layer flake, where the most prominent changes in chemical potential occur after laser writing, we calculate \( I_{PTE}/I_{PV} \approx -0.06 \) using Eq. 2. Thermalization of hot carriers therefore makes a negligible contribution to the total photocurrent generated at FeCl\(_3\)-FLG p-p’ junctions and acts in the opposite direction to dominant photovoltaic processes. Opposing photocurrents at p-p’ junctions have previously been predicted in monolayer graphene transistors with split electrostatic gates (5) and can be understood intuitively by considering that the movement of photogenerated charge carriers is governed by local gradients in chemical potential for photovoltaic currents and by local gradients in Seebeck coefficient for thermoelectric currents. Following the Mott relation \( S \approx -\sigma^{-1}(do/d\mu) \), the density states of graphene dictates that these gradients will always point in opposite directions so long as the chemical potentials on each side of a photovoltaic junction are both situated in the valence band (p-p’ junctions) or in the conduction band (n-n’ junctions) away from the charge neutrality point. As a result of these findings, we take the direction of photocurrent signals shown in Fig. 2C (where carriers drift according to the local potential gradient at p-p’ interfaces) as direct evidence of a purely photovoltaic response in laser-written FeCl\(_3\)-FLG detectors.

Through chemical functionalization, the selective quenching of thermoelectric processes in graphene could prove to be a highly useful tool for extending the use of graphene-based light sensors beyond microbolometers and modulators suitable for infrared wavelengths. Pixels of FeCl\(_3\)-FLG-based photodetectors would not require thermal isolation and could be packed to a far higher density than undoped graphene monolayers, making them well-suited for imaging applications over a broad spectral range.

**Extraordinary LDR**

The purely PV response in FeCl\(_3\)-FLG detectors is characterized by an extraordinary LDR. The noise-equivalent power (NEP) of our device was measured to be 4 kW/cm\(^2\) (see section S2.2), thus resulting in an LDR of 44 dB. This is 4500 times larger than that of previously reported graphene photodetectors (LDR \( \approx 7.5 \text{ dB} \) (3)) and ~800 times larger than that of other functionalized graphene devices (LDR \( \approx 15 \text{ dB} \) (13)). In Table S1, we show a comparison of the maximum saturation power and LDR for different devices reported in literature (see also section S2.3 for a comparative study of detectors).

To further assess the suitability of FeCl\(_3\)-FLG for optoelectronic applications, we have characterized the photoresponse at these p-p’ junctions over a wide range of light intensities and wavelengths. Figure 3B shows the power dependence of photocurrent measured at a p-p’ junction in FeCl\(_3\)-FLG for various wavelengths of incident light ranging from UVA (375 nm) to red (685 nm). Fits of the power exponent at each wavelength give the following: \( \alpha_{375} = 0.99 \pm 0.01 \), \( \alpha_{473} = 1.05 \pm 0.06 \),
The spatial resolution of FeCl₃ displacement at the engineered p-p' junctions is determined by the profile of the laser spot used for patterning. In far-field optical microscopy, spot sizes are dictated by the Abbe diffraction limit [\( \sim \lambda/(2NA) \)], where NA is the numerical aperture of the objective. To explore the density to which graphene-based imaging pixels may be packed in the absence of hot-carrier effects, we use scattering-type near-field optical microscopy (s-SNOM; see Materials and Methods) to define photoactive junctions below the Abbe limit. This technique has been used extensively to study the plasmonic (29) and optoelectronic (30) response of graphene-based devices. Figure 4 (A to C) shows photocurrent maps using a \( \lambda = 10 \mu \text{m} \) excitation source taken before and after FeCl₃ displacement by a \( \lambda = 632 \text{ nm} \) laser. Planar junctions exhibiting a photovoltaic response are readily defined with a peak-to-peak separation of just 250 nm (Fig. 4F), while concurrent topography mapping (Fig. 4, D and E) indicates that the flake surface remains undamaged. Furthermore, the photocurrent is stronger near the edges of the flake, suggesting that the deintercalation process is due to the displacement of FeCl₃ molecules in the plane of graphene that are removed from the edges. The absorption of photons with energy \( E \ll 2\mu \text{m} \) in FeCl₃-FLG highlights the role of transitions to the \( \pi \) band from localized states introduced by FeCl₃, as predicted by density functional theory calculations (31). This prevents Pauli blocking of long wavelengths and maintains a broadband spectral response, up to MIR wavelengths, in these novel photodetectors.

**Below the diffraction limit**

The spatial resolution of FeCl₃ displacement at the engineered p-p' junctions is determined by the profile of the laser spot used for patterning. In far-field optical microscopy, spot sizes are dictated by the Abbe diffraction limit [\( \sim \lambda/(2NA) \)], where NA is the numerical aperture of the objective. To explore the density to which graphene-based imaging pixels may be packed in the absence of hot-carrier effects, we use scattering-type near-field optical microscopy (s-SNOM; see Materials and Methods) to define photoactive junctions below the Abbe limit. This technique has been used extensively to study the plasmonic (29) and optoelectronic (30) response of graphene-based devices. Figure 4 (A to C) shows photocurrent maps using a \( \lambda = 10 \mu \text{m} \) excitation source taken before and after FeCl₃ displacement by a \( \lambda = 632 \text{ nm} \) laser. Planar junctions exhibiting a photovoltaic response are readily defined with a peak-to-peak separation of just 250 nm (Fig. 4F), while concurrent topography mapping (Fig. 4, D and E) indicates that the flake surface remains undamaged. Furthermore, the photocurrent is stronger near the edges of the flake, suggesting that the deintercalation process is due to the displacement of FeCl₃ molecules in the plane of graphene that are removed from the edges. The absorption of photons with energy \( E \ll 2\mu \text{m} \) in FeCl₃-FLG highlights the role of transitions to the \( \pi \) band from localized states introduced by FeCl₃, as predicted by density functional theory calculations (31). This prevents Pauli blocking of long wavelengths and maintains a broadband spectral response, up to MIR wavelengths, in these novel photodetectors.

**CONCLUSIONS**

In conclusion, laser patterning is an elegant method for creating photoresponsive junctions in intercalated few-layer graphene. Photoresponsive
junctio ns in FeCl₃-FLG are engineered on the submicrometer scale and remain highly stable under atmospheric conditions and intense light exposure. This presents a unique opportunity relative to other methods of chemical functionalization, whereby photocurrent mechanisms are reliably pinned to produce a linear response over broad ranges of power and wavelength with no requirement for encapsulation from the environment. These junctions show an extraordinary LDR up to 44 dB, more than 4500 times larger than that of other graphene photodetectors, which can operate at incident optical powers up to 10⁵ kW/cm² in the whole visible range, in the near-UV, and at MIR wavelengths. Further enhancements in responsivity can be achieved through the use of an increased number of intercalated graphene layers and optimization of the deintercalation process to maximize the chemical potential gradient at p-p' junctions. Uniform intercalation of FeCl₃ throughout large-area graphene films of a uniform layer number will be crucial for implementing these findings in practical applications. To this end, intercalation of large-area chemical vapor deposition (CVD)-grown graphene has already been demonstrated (15, 32, 33), and roll-to-roll processing of graphene (34) is readily applicable to intercalated films. Compact pixel arrays could be realized using vertical circuitry equivalent to buried channels in complementary metal-oxide semiconductor technology, where vias connect between pixels on the substrate surface and laterally running interconnects dispersed over several buried levels. These findings provide exciting prospects for light detection in laser-induced plasmas, UV photocatalytic water sanitation processes, and high-precision manufacturing. In these environments, these novel sensors could eliminate the need for attenuating optics in the detection of ultrabright light signals with high spatial resolution.

MATERIALS AND METHODS

Device fabrication

Few-layer graphene flakes were mechanically exfoliated from natural graphite on a p-doped silicon substrate with a 280-nm surface oxide. Intercalation with FeCl₃ was conducted in a two-zone furnace using a previously demonstrated vapor transport method (14). Electrical contacts to the flakes were defined by standard electron-beam lithography, thermal deposition of Cr/Au (5/50 nm), and lift-off in acetone.

Raman spectroscopy

Raman spectroscopy measurements used to characterize the degree of intercalation in FeCl₃-FLG were performed in atmosphere and at room temperature (see the Supplementary Materials). Raman spectra were acquired with a Renishaw spectrometer equipped with a 532-nm laser focused to a 1.0-μm spot through a 50× objective lens. An incident power of 1 mW was used for all measurements, and spectra were recorded with a 2400 g/mm grating. A charge-coupled device acquisition time of 5 s was used.

Photocurrent measurements

A continuous-wave laser beam from a multiwavelength (Coherent OBIS 375LX, 473LS, 514LX, 561LS and Omicron LuxX 685) solid-state laser diode array was focused onto the sample through a 50× lens, producing a spot size of 1.0 μm. A high-resolution microscope stage (minimum step size of 0.05 μm) was used to produce spatial maps of the photocurrent. Electrical measurements were performed in short-circuit (zero bias) configuration using a DL Instruments Model 1211 current amplifier connected to a Signal Recovery model 7124 digital signal processing lock-in amplifier. The lasers were modulated at a frequency of 73.3 Hz with a transistor-transistor logic signal from a direct digital synthesizer function generator, which was used as a reference signal for the lock-in. All measurements were performed under ambient conditions (T = 300 K, P = 1 atm) in air. The laser power was varied from 1.5 μW to 1 mW by analog modulation of the laser diodes and the use of neutral density filters along the beam path. All the devices studied have been measured in air over a time scale longer than 1 year, during which no change in the photoresponse was observed.

LDR calculation

The LDR is defined as

$$\text{LDR} = 10 \times \log_{10} \left( \frac{P_{\text{sat}}}{\text{NEP}} \right) \text{[dB]}$$

where the NEP is defined as the power at which the signal-to-noise ratio has a value of 1. The NEP can be measured directly or computed as

$$\text{NEP} = \frac{S_j}{\mathbb{R}} \left[ W / \sqrt{Hz} \right],$$

where $S_j$ is the root mean square current noise (in A/√Hz), and $\mathbb{R}$ is the responsivity of the photodetector (in A/W).

s-SNOM measurements

s-SNOM involves focusing a laser onto a metallized atomic force microscope (AFM) tip, which creates a strong, exponentially decaying field at its apex. The tip is then scanned across the sample, operating in tapping mode, allowing parameters, including topography and scattered light emission, to be measured with subwavelength resolution (35–37). If the device is contacted as in this work, the local photocurrent, produced by the light focused at the tip, could be measured with the same resolution. s-SNOM measurements were performed using a commercially available system from Neaspec GmbH. The AFM tips used were commercially available metal-coated tips with average radii of 25 nm. Our system was equipped with a tunable CO₂ laser and a visible wavelength HeNe laser. Here, the CO₂ laser was used to probe the optical near-field signal of our samples, whereas the visible laser was used only for laser patterning of the p-p' junctions in our devices. Concurrent photocurrent and AFM topography measurements were performed in short-circuit configuration using the CO₂ laser before and after laser patterning.

SUPPLEMENTARY MATERIALS

Supplementary material for this article is available at http://advances.sciencemag.org/cgi/content/full/3/5/e1602617/DC1

section S1. Supplementary data on laser irradiation

section S2. Supplementary photocurrent measurements

section S3. Power dependence of the photothermoelectric and photovoltaic effects

section S4. Estimation of chemical potential and conductivity for decoupled graphene layers

section S5. Physical explanation for a purely photovoltaic response

section S6. Correction of responsivity spectra for substrate reflections

fig. S1. Infrared stacking order of four-layer FeCl₃-FLG

fig. S2. Calibration of laser-induced displacement of FeCl₃

fig. S3. Bandwidth of a laser-written FeCl₃-FLG junction device.

fig. S4. NEP of laser-written FeCl₃-FLG junction device.

fig. S5. Characterization of supported pristine graphene devices.

fig. S6. Additional measurements of photocurrent in supported pristine graphene devices.

fig. S7. Photoresponse at p-p' junction in FLG.

fig. S8. Calculation of the carrier concentration and chemical potential at p-p' interfaces of FeCl₃-FLG.

fig. S9. Direction of photocurrent at p-p' junctions of FeCl₃-FLG.

fig. S10. Correction of spectral responsivity for substrate reflections.

table S1. LDR of graphene and functionalized graphene devices.
REFERENCES AND NOTES
1. F. H. L. Koppens, T. Mueller, P. Avouris, A. C. Ferrari, M. S. Vitiello, M. Polini, Photodetectors based on graphene, other two-dimensional materials and hybrid systems. Nat. Nanotechnol. 9, 780–793 (2014).
2. N. Liu, H. Tian, G. Schwartz, J. B.-H. Tok, T.-L. Ren, Z. Bao, Large-area, transparent, and flexible infrared photodetector fabricated using P-N junctions formed by N-doping chemical vapor deposition grown graphene. Nano Lett. 14, 3702–3708 (2014).
3. T. Mueller, F. Xia, P. Avouris, Graphene photodetectors for high-speed optical communications. Nat. Photonics 4, 297–301 (2010).
4. K. J. Tielrooij, M. Massicotte, L. Piatkowski, A. Woessner, Q. Ma, P. Jarillo-Herrero, N. F. van Hulst, F. H. L. Koppens, Hot-carrier photocurrent effects at graphene-metal interfaces. J. Phys.: Condens. Matter 27, 164207 (2015).
5. J. C. W. Song, M. S. Rudner, C. M. Marcus, L. S. Levitov, Hot carrier transport and photocurrent response in graphene. Nano Lett. 11, 4688–4692 (2011).
6. M. C. Lemme, F. H. L. Koppens, A. L. Fallk, M. S. Rudner, H. Park, L. S. Levitov, C. M. Marcus, Gate-activated photoresponse in a graphene p-n junction. Nano Lett. 11, 4134–4137 (2011).
7. N. M. Gabor, J. C. W. Song, Q. Ma, N. L. Nair, T. Taychatanapat, K. Watanabe, T. Taniguchi, L. S. Levitov, P. Jarillo-Herrero, Hot carrier-assisted intrinsic photoresponse in graphene. Science 334, 648–652 (2011).
8. M. F. Cracium, I. Khrapach, M. D. Barnes, S. Russo, Properties and applications of chemically functionalized graphene. J. Phys.: Condens. Matter 25, 423201 (2013).
9. M. W. Graham, S.-F. Shi, D. C. Ralph, J. Park, P. L. McEuen, Photocurrent measurements of supercolllision cooling in graphene. Nat. Phys. 9, 103–108 (2013).
10. D. B. Farmer, Yu-M. Lin, A.-A. Ali, A. Phaedon, Behavior of a chemically doped graphene junction. Appl. Phys. Lett. 94, 213106 (2009).
11. T. Lohmann, K. von Klitzing, J. H. Smet, Four-terminal magneto-transport in graphene p-n junctions created by spatially selective doping. Nano Lett. 9, 1973–1979 (2009).
12. L. Lin, X. Xu, J. Yin, J. Sun, Z. Tan, A. L. Koh, H. Wang, H. Peng, Y. Chen, Z. Liu, Tuning chemical potential difference across alternately doped graphene p-n junctions for high-efficiency photodetector. Nano Lett. 16, 4094–4101 (2016).
13. S. Wang, Y. Sekine, S. Suzuki, F. Maeda, H. Hibino, Photocurrent generation of a single gate graphene p-n junction fabricated by interfacial modification. Nanotechnology 26, 385203 (2015).
14. I. Khrapach, F. Withers, T. H. Bointon, D. K. Polyushkin, W. L. Barnes, S. Russo, M. F. Cracium, Novel highly conductive and transparent graphene-based conductors. Adv. Mater. 24, 2844–2849 (2012).
15. T. H. Bointon, G. F. Jones, A. De Sanctis, R. Hill-Pearce, M. F. Cracium, S. Russo, Large-area functionalized CVD graphene for work function matched transparent electrodes. Sci. Rep. 5, 16464 (2015).
16. D. J. Whelen, T. H. Bointon, T. Booth, P. Baggild, M. Felicia Cracium, S. Russo, Unforeseen high temperature and humidity stability of FeCl3 intercalated few layer graphene. Sci. Rep. 5, 7609 (2015).
17. C. O. Kim, S. Kim, D. H. Shin, S. S. Kang, J. M. Kim, C. W. Jung, S. S. Joo, S. J. Lee, J. H. Kim, S.-H. Choi, E. Hwang, High photoresponsivity in an all-graphene p-n vertical junction photodetector. Nat. Commun. 5, 3249 (2014).
18. K. J. Tielrooij, L. Piatkowski, M. Massicotte, A. Woessner, Q. Ma, Y. Lee, K. S. Myhro, C. N. Lau, P. Jarillo-Herrero, N. F. van Hulst, F. H. L. Koppens, Generation of photovoltage in graphene on a femtosecond timescale through efficient carrier heating. Nat. Nanotechnol. 10, 437–443 (2015).
19. V. Patil, A. Capone, S. Strauf, E.-H. Yang, Improved photoresponse with enhanced photoelectric contribution in fully suspended graphene photodetectors. Sci. Rep. 3, 2791 (2013).
20. C.-H. Liu, Y.-C. Chang, T. B. Norris, Z. Zhong, Graphene photodetectors with ultra-broadband and high responsivity at room temperature. Nat. Nanotechnol. 9, 273–278 (2014).
21. M. Lazeri, F. Mauri, Nonadiabatic Kohn anomaly in a doped graphene monolayer. Phys. Rev. Lett. 97, 266407 (2006).
22. A. Das, S. Pissanas, B. Chakraborty, S. Piscanek, S. K. Saha, U. V. Waghmare, K. S. Novoselov, H. R. Krishnamurthy, A. K. Geim, A. C. Ferrari, A. K. Sood, Monitoring dopants by Raman scattering in an electrochemically top-gated graphene transistor. Nat. Nanotechnol. 3, 210–215 (2008).
23. B. Wisotzki, A. H. MacDonald, Electronic cooling in graphene. Phys. Rev. Lett. 102, 206410 (2009).
24. J. C. W. Song, M. Y. Reizer, L. S. Levitov, Disorder-assisted electron-phonon scattering and cooling pathways in graphene. Phys. Rev. Lett. 109, 106602 (2012).
measurements and performed the analysis and interpretation of the photocurrent response with key contributions from F.H.L.K. and F.B. The s-SNOM measurements were performed by F.B. with the assistance of A.D.S. A.D.S. and G.F.J. wrote the manuscript with contributions and ideas from all the authors. M.F.C. and S.R. supervised the whole project. Competing interests: The authors declare that they have no competing interests. Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the main text and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors. Correspondence and requests for materials should be addressed to S.R.

Citation: A. De Sanctis, G. F. Jones, D. J. Wehenkel, F. Bezares, F. H. L. Koppens, M. F. Craciun, S. Russo, Extraordinary linear dynamic range in laser-defined functionalized graphene photodetectors. Sci. Adv. 3, e1602617 (2017).