Multiple hot-carrier collection in photo-excited graphene Moiré superlattices

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In conventional light-harvesting devices, the absorption of a single photon only excites one electron, which sets the standard limit of power-conversion efficiency, such as the Shockley-Queisser limit. In principle, generating and harnessing multiple carriers per absorbed photon can improve efficiency and possibly overcome this limit. We report the observation of multiple hot-carrier collection in graphene/boron-nitride Moiré superlattice structures. A record-high zero-bias photoresponsivity of 0.3 A/W (equivalently, an external quantum efficiency exceeding 50%) is achieved using graphene’s photo-Nernst effect, which demonstrates a collection of at least five carriers per absorbed photon. We reveal that this effect arises from the enhanced Nernst coefficient through Lifshitz transition at low-energy Van Hove singularities, which is an emergent phenomenon due to the formation of Moiré minibands. Our observation points to a new means for extremely efficient and flexible optoelectronics based on van der Waals heterostructures.

INTRODUCTION

The Shockley-Queisser efficiency limit for converting light into electricity exists mainly as a result of the spectral loss of photon energy below and above the absorber’s bandgap. For instance, any excess energy of an above-bandgap excitation will dissipate as loss in conventional devices. However, if this excess energy can be used to excite secondary carriers, leading to carrier multiplication, it is possible to outperform the standard limit (1). The realization of this goal hinges on the identification of suitable physical systems, where both the multiplication process occurs and the subsequent carrier extraction efficiency is high. Among the promising candidates, such as quantum dots or carbon nanotubes, graphene has an outstanding potential because of its broadband absorption, ultrahigh carrier mobility, and structural flexibility. Recent ultrafast optical and photoemission measurements have revealed multiple hot-carrier generation per photon excitation in moderately doped graphene due to strong carrier-carrier scattering (2–6). In principle, this process minimizes spectral loss because graphene has zero gap and all the absorbed photons release their energy efficiently by generating useful hot carriers, making graphene an excellent platform for light-harvesting. However, effective conversion of these hot carriers into current has not been shown in graphene optoelectronic devices, which have typical zero-bias photoresponsivities of less than 10 mA/W (7), implying that there is less than one collected carrier per absorbed photon.

Here, we demonstrate the collection of multiple hot carriers upon the absorption of one photon in graphene by creating critical spectral points in the electronic bands via engineered van der Waals heterostructures. In general, Fermi surface topology at band critical points can undergo sudden changes, giving rise to electronic topological transition (8), or Lifshitz transition. This effect can cause anomalies in material properties, such as conductivity, specific heat, and thermoelectric coefficients (8). The latter is particularly important to graphene’s optoelectronic behavior because its photocurrent generation is dominated by photo-thermoelectric effects (9–11). Away from the Dirac points (DPs), the energy spectrum of graphene contains such critical points, at which Van Hove singularities (VHSs) appear (12). However, the extremely high doping required to reach these VHSs has prevented their experimental access in pristine graphene. Alternatively, the formation of Moiré superlattices in twisted graphene bilayers (13) and graphene on hexagonal boron-nitride (h-BN) heterostructures (14–18) generates electronic minibands that mimic graphene’s energy spectrum but with a reduced energy scale, providing a unique opportunity to study a variety of physical phenomena that were previously inaccessible (14–16, 19, 20). In particular, the long-wavelength Moiré superlattice formed in aligned graphene/h-BN heterostructures (Fig. 1, A and B) simultaneously achieves high-degree band engineering and excellent transport performance (14–16). It has been demonstrated that this superlattice can open up a bandgap in graphene (16, 19), can make the two degenerate electronic valleys topologically distinguishable (20), can generate secondary DPs (sDPs) (18), and can give rise to a fractal quantum structure known as Hofstadter’s butterfly (14–16). Here, we reveal the remarkable influence of the emergent low-energy VHSs in the superlattice minibands on graphene’s optoelectronic response, yielding a highly efficient photocurrent generation that may lead to a new type of graphene optoelectronics.

RESULTS

Our devices were made with graphene encapsulated between h-BN sheets sitting on a graphite gate, using recently developed polymer-free transfer techniques (21). In each device, a large area (~100 μm²) with a clean region in the heterostructure was achieved and fabricated into an edge-contacted Hall-bar geometry (21). This enabled spatially resolved photocurrent measurements on a high-quality sample with characterization of both longitudinal and Hall resistivity. Figure 1 (A and C) shows

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the schematic diagram and an optical micrograph of a fabricated device. The room temperature mobility of such devices is phonon-limited (21) and typically 100,000 cm²/(V·s) at a carrier density of ~10¹² cm⁻². Our measurements were performed at 4.2 K with tunable magnetic field B perpendicular to the sample unless otherwise mentioned.

Figure 1D shows the longitudinal resistance Rₓₓ of the device, as a function of graphite back-gate voltage Vᵔ measured at B = −50 mT. The peak with a resistance of ~80 kilohm at Vᵔ ≈ −0.1 V corresponds to the main DP. Two additional resistance peaks are present at Vᵔ = −4.7 V (stronger) and +4.4 V (weaker), representing the sDPs, the hallmarks of the formation of a long-wavelength Moiré superlattice (14–17). Following Dean et al. (15), we determine the Moiré wavelength to be ~14 nm in this device.

The photocurrent measurements were performed under continuous wave (CW) laser excitation (660 nm) with a beam spot size of about 2 µm on the sample. While grounding the source and floating all the voltage probes, we collected photocurrent from the drain contact (Fig. 1A) (see Materials and Methods). Figure 1E plots the observed photocurrent as a function of Vᵔ under weak magnetic fields when placing the laser spot at a selected graphene edge (Fig. 1A). The incident power was set at 1 µW before the objective. We found that the observed photocurrent has a strong dependence on Vᵔ. For a slightly nonzero B (~50 mT), a greatly enhanced photocurrent, indicated by the red arrows, is observed nearby both electron- and hole-side sDPs (e-sDP and h-sDP, respectively). We have repeated the observation of this enhancement in a second superlattice device with a different Moiré wavelength (~10 nm), as shown in fig. S1. These photocurrents switch direction when B is reversed. They appear only when pumping near the device edges and flow oppositely at opposite edges. This chiral edge nature is clearly revealed through a spatially resolved scanning photocurrent map (Fig. 1F) at a selected gate voltage.

Such photocurrents have been attributed to the photo-Nernst effect (22). Because of the weak electron-phonon interactions in graphene, optically excited electrons are known to release their energy at a sub-picosecond time scale by generating multiple hot carriers near the Fermi surface (2, 23, 24). These processes, leading to photo-thermoelectricity (9–11), are largely responsible for the photocurrent generation in various graphene optoelectronic devices (7). In our case, because the laser beam is focused onto the sample edge, a temperature gradient of hot carriers forms from edge to bulk. Under the perpendicular magnetic field, a net transverse magneto-thermoelectric current, or Nernst current, can thus flow along the edge (22).

What is unique in our observation is that the photo-Nernst current is drastically enhanced near the sDPs (Fig. 1E). To understand this, we carefully inspect the Moiré superlattice electronic band structure (25). Although the exact parameters in the Hamiltonian vary from device to
device, a general treatment considering the Moiré superlattice with zero twist angle (25) can give an intuitive picture that explains our observation. Figure 2A plots the calculated lowest four bands at one valley, and the dashed black arrows indicate sDPs in two selected bands. The corresponding electronic density of states (DOS) is shown in Fig. 2B, where DOS minima feature the DP and sDPs. e-sDPs and h-sDPs are each flanked by two pronounced DOS peaks (labeled a to d). Those four peaks have been identified as VHSs existing in the Moiré minibands (25, 26).

Our calculation suggests that these VHSs arise from saddle point formation in the Moiré minibands, indicated by the white solid arrows in Fig. 2A. In Fig. 2C, we plot the constant energy contour near saddle point b, where one can clearly see the transition from sDP (μ points, center of the blue contour) to DP (center of the red contour). The saddle point singularities are located in between μ and λ points, which are the local energy minima at the corner of the superlattice Brillouin zone (sBZ), as shown by the zoomed-in plot in Fig. 2C. Similar electronic structures can also be found for saddle points a, c, and d (Fig. S2).

These band singularities feature Lifshitz transitions, where the electron Fermi surface has a sudden topology change. One direct consequence of such Lifshitz transitions is the orbital switching from electron-like to hole-like (27). This is exactly what happens in the Moiré minibands. Figure 3A illustrates the evolution of the simulated Fermi surface (see Materials and Methods) as the Fermi energy increases from h-sDP to DP, passing through saddle point b (Fig. 2B). Directly above the h-sDP, there are six electron-like Fermi pockets at μ points. As the Fermi energy increases, the Fermi surface enlarges but remains electron-like, although new electron-like pockets at λ points appear. At the VHS, the separated Fermi pockets connect, after which a single hole-like pocket forms at the sBZ center.

It has been established that Lifshitz transition causes anomalies in a wide range of material properties, which can be used to identify the appearances of VHSs. In our case, this can be seen in the transverse ($\sigma_{xy}$) and longitudinal ($\sigma_{xx}$) conductivities. Figure 3B shows $\sigma_{xy}$ at 455 mT as a function of $V_g$. There are sudden sign changes in $\sigma_{xy}$ near the sDPs, showing that the carriers experience orbital switching upon slightly tuning the Fermi energy (Fig. 3A). Accompanying these sign changes, pronounced peaks in $\sigma_{xx}$ (Fig. 3C) also appear, particularly the b and c peaks that can be easily identified. These observations reveal the formation of VHSs. Peaks a and d are not observed. We suspect that they appear outside the achievable range of gate voltage. Similar behaviors in conductivities have been theoretically discussed in pristine graphene (28). However, in such cases, extreme doping is required to tune the Fermi level up to VHSs, preventing experimental observations.

Intriguingly, it is such a Lifshitz transition that leads to the enhanced photo-Nernst current. Figure 3D plots the observed photocurrent $I_{pc}$ as a function of gate voltage. One can see that the conductivity peaks map one to one with the enhanced features in the photocurrent anomalies to the VHSs. The slight offset in gate voltage at peak b between $I_{pc}$ and $\sigma_{xx}$ may be due to the optical gating of graphene through BN (29). We note that near e-sDP, $I_{pc}$ appears with opposite polarity with respect to the response at VHSs. The nature of this current is not clear; however, our simulation of band structures implies that this could result from the presence of two sets of closely located Dirac-like points with broken inversion symmetry (fig. S3).

To further reveal the underlying physics of $I_{pc}$, we formulate the short-circuit current by $I_{pc} = S_{xy} (\Delta T_{el}) / \rho_{xx} \approx S_{xy} (K_{th} \rho_{xx})$, where $S_{xy}$ is the transverse thermoelectric power, $\langle \Delta T_{el} \rangle$ is the average electronic

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**Fig. 2. VHSs in Moiré minibands.** (A) Simulated lowest four bands in the k valley for the graphene/BN superlattice with zero twist angle. e-sDPs and h-sDPs are indicated by the dashed black arrows. The solid white arrows locate the saddle points in the first hole and second electron bands. (B) The electronic DOS corresponding to the simulated energy bands, showing the saddle point VHSs labeled a to d in (A). (C) Constant energy contour of the first hole band in momentum space near the saddle point singularities. The dashed hexagonal lines indicate the sBZ, which is further shown at the top right inset. Red (blue) color denotes the Fermi surface approaching DP (sDP). In addition to the sDP at μ points, another local energy minimum is located at λ symmetry points. The saddle points are located in between μ and λ points, as depicted by the zoomed-in plot at the bottom right. The formation of saddle point VHSs in superlattice minibands appears in all four bands in (A).
temperature difference from hot center to cold bulk, \( \rho_{xx} \) is the longitudinal resistivity, and \( K_{th} \) is the electron thermal conductivity. If the Wiedemann-Franz law holds, then \( K_{th} \approx \frac{1}{\rho_{xx}} \). As a result, \( I_{pc} \approx S_{xy} \equiv NB \), where \( N \) is the Nernst coefficient and determines the photocurrent response. At the onset of the Lifshitz transitions, the thermoelectric response is significantly enhanced, leading to a large photo-Nernst effect. To reveal this, we compute \( S_{xy} \) using the standard Mott formula (30, 31),

\[
S_{xy} \propto \left( \frac{\sigma}{E_f} \right)_{xy} + \left( \frac{1}{\sigma} \right)_{xy} \left( \frac{\partial \sigma}{\partial E} \right)_{xy},
\]

where \( E_f \) is the Fermi energy.

The calculated \( S_{xy} \) in Fig. 3E matches \( I_{pc} \) well, except for the exact DP and h-sDP, where the Mott formula might be invalid (31, 32). This agreement between \( S_{xy} \) and \( I_{pc} \) confirms the Nernst nature of photocurrent. Moreover, we can conclude that the enhanced \( I_{pc} \) is a direct manifestation of the large Nernst coefficient at the VHSs, enabling very efficient extraction of the photo carriers in graphene Moiré superlattices.

Remarkably, the observed photocurrent corresponds to a giant photoresponsivity \( \zeta \). As shown in Fig. 1E, at \( B = -50 \) mT, the maximum photocurrent already appears as large as 200 nA with an incident power of about 1 \( \mu \)W, which corresponds to \( \zeta = 0.2 \) A/W, which is two orders of magnitude larger than the previously reported photo-Nernst current (22) and 20 times larger than the highest reported values in graphene photodetectors under short-circuit and normal-incidence conditions (7). Figure 4 shows \( \zeta \) at \( V_g = 4 \) V as a function of \( B \) field (see also fig. S4). One can see that \( \zeta \) increases linearly below 0.1 T and then slightly decreases at higher fields, indicating a transition from the classical to a quantum regime. The solid line is a guide to the eye to the linear response. The data are taken at \( V_g = 4 \) V.
decrease in $B$ at high field implies the transition of the system into a quantum regime (fig. S4).

Another figure of merit of an optoelectronic device is its external quantum efficiency $\eta$, the ratio between the number of collected carriers and that of the incident photons. It can be formulated by $\eta = \frac{I_{pc}}{I_{0}} = \zeta_{hole}$, where $I_{pc}$ is the photocurrent amplitude, $p$ is the excitation power, $h\nu$ is the photon energy, and $e$ is the electron charge. It yields a maximum $\eta$ of more than 50% in this device. Consequently, the internal quantum efficiency in this device greatly exceeds unity because graphene’s absorption coefficient is much less than one. Although the superlattice structure may modulate its exact value, $\alpha$ is expected to be on the order of 2.3%, with an upper limit of about 10% (33). This implies that upon the absorption of one photon, at least $\eta/\alpha > 5$ electrons are collected. Considering that the laser only illuminates the graphene edge, the effective excitation power on the sample is smaller than measured. We expect that the actual captured hot carriers per photon absorption are much larger than the number estimated above.

DISCUSSION

In summary, our results point to a unique way of harnessing VHSs emergent in Moiré band engineering for converting photo-excited hot carriers into current in van der Waals heterostructures. The Lifshitz transitions at miniband VHSs facilitate enhanced thermoelectricity when Fermi level is aligned with the singularity, leading to the multiple hot-carrier collection and the subsequent giant photocurrent generation. Although the present study uses visible light, we also expect similar effects at other wavelengths, such as in near- and mid-infrared regions, as long as the photo-excitation is above the sDPs.

In the current device geometry, we have exploited the photo-Nernst effect, where a small magnetic field is required to generate current. On one hand, fabrication of the graphene/h-BN superlattice on a ferromagnetic layer may overcome this limitation (34), making it possible to create optoelectronic devices based on the photo-Nernst effect. On the other hand, the photo-Nernst geometry is, in principle, not necessary. Future work may develop devices based on p-n junctions built on the Moiré superlattice structure, where the effect of VHSs on zero-field thermoelectric coefficient is also expected. Another possible limitation is the need for low temperature. The reduced carrier mobility and broadened VHS spectrum at high temperatures may potentially affect the performance of the device. We anticipate that further device engineering to optimize graphene’s electronic and thermal properties will be necessary for possible multiple hot-carrier collection at room temperature.

MATERIALS AND METHODS

Photocurrent measurements

In the measurements, a 660-nm CW laser was focused on the sample, with a spot size of about 2 μm, using an optical microscope objective (90% transmission). Both sample and objective were loaded together into a superconducting magnet (17.5 T). The temperature was held at 4.2 K. The sample was mounted on an attocube nanopositioning stage, which can determine the laser exposure region. The intensity of the laser beam was modulated at 800 Hz by a mechanical chopper. The photocurrent was measured by a lock-in preamplifier at a reference frequency (~800 Hz).

Resistance measurements

We measured both longitudinal $R_{xx}$ and transverse $R_{xy}$ through standard Hall-bar techniques. We applied a 1-mV excitation with 10-Hz oscillating frequency to source and measure the drain current $I_d$ by a lock-in preamplifier. The voltage drops between the two longitudinal probes $V_{xx}$ and between the two transverse probes $V_{xy}$ were recorded. Resistances were obtained using $R_{xx} = V_{xx}/I_d$ and $R_{xy} = V_{xy}/I_d$. Because the channel width and length were equal in our devices, the conductivities were obtained using $\sigma_{xx} = R_{xx}/(R_{xx}^2 + R_{xy}^2)$ and $\sigma_{xy} = -R_{xy}/(R_{xx}^2 + R_{xy}^2)$.

Band structure simulations

The miniband structure of graphene on a hexagonal substrate was calculated using the following Hamiltonian (25)

$$H = vp \cdot \sigma + u_0 E_{0} f_1 (r) + u_1 \left( \frac{E_{0}}{B} \right) \left[ I_z \times \nabla f_2 (r) \right] \sigma \tau_x + \epsilon_0 u_3 f_2 (r) \sigma \tau_z$$

where $\sigma$ and $\tau$ operate in the sublattice and valley pseudospin space, respectively. The first term describes the original DPs in pristine graphene. The next three terms with dimensionless parameters $u_0, u_1,$ and $u_3$ describe the overall scalar potential modulation, modulated nearest-neighbor hopping, and inversion-symmetric sublattice potential, respectively. The structural factors are given by $f_1 (r) = \sum_{m=0}^{5} e^{i b_m \cdot r}$ and $f_2 (r) = \sum_{m=0}^{5} (-1)^m e^{i b_m \cdot r}$, where $b_m$ are the reciprocal lattice vectors of the Moiré superlattice. The last term, proportional to $\bar{u}_3$, breaks the inversion symmetry between the A and B sublattices. We found that a small inversion-symmetry-breaking perturbation $\bar{u}_3$ is important to capture the features around the e-sDP, particularly the small bump in DOS between the VHS peaks c and d. A characteristic energy $E_{0} = \hbar \nu$ was introduced, where $\nu = |b_0| \sim (4\pi/3\alpha)(\delta^2 + \theta^2)$, with $\delta$ and $\theta$ being the ratio of lattice constants with and without substrate and $\theta$ being the twisting angle. Throughout our calculation, $\theta$ was set to zero. Diagonalizing the Hamiltonian yielded the miniband structure and the DOS. We found that the main feature of the experimental result can be qualitatively explained with only two nonzero parameters, $u_0$ and $\bar{u}_3$. The actual calculation was performed with $(u_0, u_1, \bar{u}_3, \bar{u}_3) = (-0.15, 0, 0, 0.004)$.

SUPPLEMENTARY MATERIALS

Supplemental material for this article is available at http://advances.sciencemag.org/cgi/content/full/2/5/e1600002/DC1
fig. S1. Data taken from another graphene/BN superlattice device.
fig. S2. Saddle points corresponding to VHS peaks a, c, and d.
fig. S3. Band structure at e-sDP.
fig. S4. Raw data corresponding to Fig. 4 in the main text.

REFERENCES AND NOTES

RESEARCH ARTICLE


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Data and materials availability: All data needed to evaluate the conclusions in the paper are present in the paper and/or the Supplementary Materials. Additional data related to this paper may be requested from the authors.

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