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 transitions (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 DPSs (2DPs) (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...
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 \( R_{xx} \) of the device, as a function of gate at 50 mT showing one DP and two sDPs. Inset zooms in the e-sDP peak. (E) Photocurrent generation as a function of gate under a magnetic field varying from −50 to 50 mT with a step size of 20 mT. The drain current is recorded while grounding the source, as shown in (A). Laser power is set at 1 μW before microscope objective. The red arrow indicates the enhanced photocurrent features. \( T = 4.2 \) K. (F) Typical spatially resolved scanning photocurrent map (taken at 20 K), showing the chiral edge pattern consistent with the photo-Nernst current, which is generated at the two edges with opposite signs.

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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 κ symmetry points. The saddle points are located in between μ and κ 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).

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 (σxy) and longitudinal (σxx) conductivities. Figure 3B shows σxy at 455 mT as a function of Vg. There are sudden sign changes in σxy 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 σxx (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 VSIs, preventing experimental observations.

Intriguingly, it is such a Lifshitz transition that leads to the enhanced photo-Nernst current. Figure 3D plots the observed photocurrent Ipc as a function of gate voltage. One can see that the conductivity peaks map one to one with the enhanced features in Ipc unambiguously connecting the photocurrent anomalies to the VHSs. The slight offset in gate voltage at peak b between Ipc and σxx may be due to the optical gating of graphene through BN (29). We note that near e-sDP, Ipc 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 Ipc, we formulate the short-circuit current by \( I_{pc} = S_{xy} \langle \Delta T_{el} \rangle / \rho_{xx} \approx S_{xy} / (K_{th} \rho_{xx}) \), where \( S_{xy} \) is the transverse thermoelectric power, \( \langle \Delta T_{el} \rangle \) is the average electronic
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 $K_{th} \approx 1/\rho_{xx}$. 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),

$$S_{xy} \approx (\sigma^{-1})_{xx} \left( \frac{\partial \sigma_{xx}}{\partial E} \right)_{yy} + (\sigma^{-1})_{xy} \left( \frac{\partial \sigma_{xx}}{\partial E} \right)_{yy},$$

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 µW. This 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.
and that of the incident photons. It can be formulated by quantum efficiency in the quantum regime (fig. S4).

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 in 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)

$$H = v_p \cdot \sigma + \epsilon_0 \sum_{m=0}^{5} e^{|b_m\cdot r|} f_1(r) + \epsilon_1 \sum_{m=0}^{5} e^{|b_m\cdot r|} f_2(r),$$

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 $\epsilon_0$, $\epsilon_1$, and $\epsilon_3$ describe the overall scalar potential modulation, modulated nearest-neighbor hopping, and inversion-symmetric sublattice potential, respectively. The structural factors are given by $f_1(r) = \sum_{m=0}^{5} e^{|b_m\cdot r|}$ and $f_2(r) = i \sum_{m=0}^{5} (-1)^m e^{|b_m\cdot r|}$, 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 $\epsilon_0 = h v_b$ was introduced, where $b = |b_3| \sim (4/13)\sqrt{\delta^2 + \theta^2}$, with $\delta$ 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 $(u_0, u_1, u_3, \bar{u}_3) = (-0.15, 0, 0, 0.004)$.

### Supplementary Materials

Supplementary 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


### 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**

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