High Responsivity, Large-Area Graphene/MoS$_2$ Flexible Photodetectors

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ABSTRACT: We present flexible photodetectors (PDs) for visible wavelengths fabricated by stacking centimeter-scale chemical vapor deposited (CVD) single layer graphene (SLG) and single layer CVD MoS$_2$, both wet transferred onto a flexible polyethylene terephthalate substrate. The operation mechanism relies on injection of photoexcited electrons from MoS$_2$ to the SLG channel. The external responsivity is 45.5 A/W and the internal 570 A/W at 642 nm. This is at least 2 orders of magnitude higher than bulk-semiconductor flexible membranes. The photoconductive gain is up to 4 $\times$ 10$^5$. The photocurrent is in the 0.1–100 $\mu$A range. The devices are semitransparent, with 8% absorptance at 642 nm, and are stable upon bending to a curvature of 1.4 cm. These capabilities and the low-voltage operation (<1 V) make them attractive for wearable applications.

KEYWORDS: photodetectors, graphene, MoS$_2$ heterostructures, flexible optoelectronics

Modern electronic and optoelectronic systems, such as smart phones, smart glasses, smart watches, wearable devices, and electronic tattoos, increasingly require ultrathin, transparent, low-cost, and energy efficient devices on flexible substrates. The rising demand for flexible electronics and optoelectronics requires materials that can provide a variety of electrical and optical functionalities, with constant performance upon application of strain. A wide range of optoelectronic devices on flexible substrates have been reported to date, such as photodetectors (PDs), light emitting diodes (LEDs), optical filters, optical interconnects, photovoltaic devices, and biomedical sensors.

Major challenges in the development of flexible optoelectronic devices stem from the limitations associated with the high stiffness of bulk semiconductors. In the case of flexible PDs, the current approaches primarily rely on thin ($\mu$m-thick) semiconductor membranes and compound semiconductor nanowires (NWs) mainly because of their ability to absorb light throughout the whole visible range (0.4–0.7 $\mu$m) and the possibility to adapt their fabrication techniques from rigid to plastic, or deformable substrates. One of the key parameters for PDs characterization is the responsivity. This is defined as the ratio between the collected photocurrent ($I_{ph}$) and the optical power. The responsivity is named external ($R_{ext} = I_{ph}/P_{o}$) or internal ($R_{int} = I_{ph}/P_{abs}$), whenever the incident ($P_{o}$) or absorbed ($P_{abs}$) optical power is used in the denominator. Since not all incident photons are absorbed by a PD, i.e., $P_{abs} < P_{o}$, then $R_{ext}$ is typically larger than $R_{int}$.

In flexible PDs, $R_{ext}$ up to ~0.3 A/W was reported for crystalline semiconductor membranes (InP, Ge) with integrated p–i–n junctions, showing photocurrent up to ~100 $\mu$A, with ~30% degradation upon bending at a radius $r_b$ ~ 3 cm. PDs made of a single semiconductor NW on flexible substrates demonstrated $R_{ext}$ up to ~10$^5$ A/W, for $r_b$ down to 0.3 cm. Yet, these provide limited $I_{ph}$ in the order of nA up to ~1 $\mu$A. For flexible devices exploiting NW arrays by drop-casting, rather than based on single NWs,
Figure 1. (a) Schematic SLG/MoS2 flexible PD, side-gated with a PE. (b) Picture of a typical PD, showing transparency and flexibility. (Inset) Optical image of 4 PDs with different channel lengths and common side gate electrode. Scale bar is 200 μm.

R_{int} degrades significantly from ∼10^5 A/W to the mA/W range, due to photocurrent loss at multiple junctions in the NW network.

Graphene and related materials (GRMs) have great potential in photonics and optoelectronics. A variety of GRM-based devices have been reported, such as flexible displays, photovoltaic modules, photodetectors, optical modulators, plasmonic devices, and ultrafast lasers. Heterostructures, obtained by stacking layers of different materials, were also explored, e.g., in photovoltaic and light emitting devices.

Flexible PDs based on GRMs were studied for ultra-violet, visible, and near-infrared bands. In these devices, different materials and heterostructures produced by mechanical exfoliation, Chemical Vapor Deposition (CVD), and liquid-phase exfoliation (LPE) were employed. The flexible PDs produced by mechanical exfoliation have a small (∼μm^2) photoactive area, and they cannot be scaled up to mass production. LPE-based PDs have low (<mA/W) responsivity. Ref 47 showed that thick (∼μm) films of chemically modified, charge-transfer optimized, LPE-produced, MoSe2 and MoS2 polymer composites can provide ∼A/W responsivity at near-infrared bands. Nevertheless, these PDs require high (>10 V) operation voltage and are not transparent. Flexible PDs at 450 nm using CVD MoS2 transistors and MoS2/WS2 heterostructures were previously reported, and PDs at 780 nm were prepared on doped SLG p–n junctions. However, these devices have responsivity in the mA/W range. CVD-based SLG/MoS2 heterostructures showed good photodetection on rigid Si/SiO2 substrates, with back-gate-dependent R_{int} ∼ 10^8 A/W for optical intensities <0.1pW/μm^2.

Here we demonstrate a polymer electrolyte (PE) gated, CVD-based, flexible PD, for visible wavelengths, with large (∼mm^2) photoactive area combined with high responsivity (>hundreds A/W), high (>80%) transparency, gate tunability, low (<1 V) operation voltage, and stable (±12%) I_{ph} upon multiple (>30) bending cycles. The device is assembled by stacking on a PET substrate a centimeter-scale CVD single layer graphene (SLG) on top of a CVD-grown single layer MoS2 (1L-MoS2). In this configuration, 1L-MoS2 acts as visible light absorber, while SLG is the conductive channel for photocurrent flow. We show that R_{int} can be increased by promoting carrier injection from 1L-MoS2 to SLG using PE gating, or by increasing the source-drain voltage. This is achieved in devices with ∼82% transparency, twice that reported for semiconductor membrane devices. We get R_{int} ∼ 570A/W for ∼0.1nW/μm^2 at 642 nm, similar to SLG/MoS2 PDs on rigid substrates operating at the same optical power. This shows that SLG/MoS2 heterostructures on PET retain their photodetection capabilities. We note that the devices from ref 48 have at least 2 orders of magnitude smaller photoactive area with respect to ours, and they are not flexible, not transparent, and require tens of volts operation, unlike the <1 V of ours. Upon bending, our PDs have stable performance for r_g down to ∼1.4 cm. This is comparable to r_g measured in semiconductor membranes PDs, which show lower (<0.3 A/W) responsivities.

Although our r_g is 1 order of magnitude larger than for flexible single NWs, the latter had at least 3 orders of magnitude smaller device areas (<5 μm^2) compared to our PDs (>0.2 mm^2). Given the responsivity, flexibility, transparency, and low operation voltage, our PDs may be integrated in wearable, biomedical, and low-power optoelectronic applications.

RESULTS

Figure 1a plots a schematic drawing of our PDs. We fabricated 4 PD arrays with 10 devices each, with channel lengths of 100 μm, 200 μm, 500 μm, and 1 mm. Each device consists of a 1L-MoS2 absorber covered by a SLG channel, clamped between source and drain electrodes. We chose PET as a flexible substrate due to its ∼90% transparency in the visible range and ability to withstand solvents (e.g., acetone and isopropyl alcohol) commonly used in the transfer processes of layered materials grown by CVD (e.g., transfer of SLG grown on Cu). A 1L-MoS2 is used as absorber in order to preserve >80% transparency, considered suitable by industry for wearable applications. Figure 1b. The SLG/1L-MoS2 heterostructure is gated using a PE.

The operation principle of our devices is depicted in Figure 2. For energy bands alignment, the electron affinity of 1L-MoS2 and the Dirac point of SLG are assumed to be ~4–4.2 eV and ~4.6 eV, respectively. We also assume SLG to be initially p-doped (Figure 2a), as reported in previous works involving SLG transferred on PET. At zero voltage the device is in thermodynamic equilibrium with a constant Fermi level and zero current flow between the layers. During illumination and photon absorption in MoS2 part of the photogenerated electrons would be injected from the 1L-MoS2 conduction band into the lower energy states in p-doped...
SLG,\textsuperscript{48} leaving behind the uncompensated charge of photo-generated holes. The latter would be trapped in 1L-MoS\textsubscript{2} and act as an additional positive gate voltage, $V_{GS}$, applied to the SLG channel, resulting in a shift of the charge neutrality point ($V_{CNP}$) to more negative voltages. The injected electrons from 1L-MoS\textsubscript{2} would occupy energy states above $E_F$ (Figure 2b), thus reducing the hole concentration and decreasing the hole current in the SLG channel. Electron injection can be further promoted by gating. When a negative $V_{GS}$ is applied, higher p-doping of the SLG channel would induce a stronger electric field at the SLG/1L-MoS\textsubscript{2} interface,\textsuperscript{48} thus favoring electron transfer from 1L-MoS\textsubscript{2} (Figure 2b). Hence, for negative $V_{GS}$, $R_{\text{ext}}$ is expected to increase, due to injection of more photoelectrons to SLG and consequent more pronounced current reduction. The opposite should happen for positive $V_{GS}$, where the gate-induced negative charge in SLG would reduce the p-doping and shift $E_F$ toward the Dirac point. In this regime, the transferred electrons would increase the free carrier concentration in the n-doped channel, hence only minor increments of $R_{\text{ext}}$ and $I_{\text{ph}}$ are expected.

Our devices are built as follows: 1L-MoS\textsubscript{2} is epitaxially grown by CVD on c-plane sapphire substrates,\textsuperscript{61} while SLG is grown on a 35 $\mu$m Cu foil, following the process described in refs 51 and 62 (see Methods for details). Prior to assembling the SLG/MoS\textsubscript{2} stack, the quality and uniformity of MoS\textsubscript{2} on sapphire and SLG on Cu are inspected by Raman spectroscopy and photoluminescence (PL), using a Horiba Jobin Yvon HR800 spectrometer equipped with a 100$\times$ objective. The laser power is kept below 100 $\mu$W (spot size <1 $\mu$m) to avoid possible heating effects or damage. Figure 3a (green curve) plots the Raman spectrum of CVD MoS\textsubscript{2} on sapphire for 514 nm excitation. The peak at $\sim$385 cm$^{-1}$ corresponds to the in-plane $(E_{2g}^{1})$ mode,\textsuperscript{63,64} while that at $\sim$404 cm$^{-1}$ is the out of plane $(A_{1g})$ mode,\textsuperscript{63,64} with full width at half-maximum FWHM $(E_{2g}^{1})$ = 2.5 and FWHM$(A_{1g})$ = 3.6 cm$^{-1}$, respectively. The $E_{2g}^{1}$ mode softens, whereas the $A_{1g}$ stiffens with increasing layer thickness,\textsuperscript{65,66} so that their frequency difference can be used to monitor the number of layers.\textsuperscript{65} The peak position difference $\sim$20 cm$^{-1}$ is an indicator of 1L-MoS\textsubscript{2}.\textsuperscript{65} The peak at $\sim$417 cm$^{-1}$ (marked by an asterisk in Figure 3a) corresponds to the $A_{1g}$ mode of sapphire.\textsuperscript{67}
The Raman spectrum measured at 514 nm of SLG on Cu is shown in Figure 3b (magenta curve). This is obtained after the removal of the background PL of Cu. The two most intense features are the G and the 2D peak, with no significant D peak. The G peak corresponds to the E_{2g} phonon at the Brillouin zone center. The D peak is due to the breathing modes of sp² rings and requires a defect for its activation by double resonance. This is always seen, even when no D peak is present, since no defects are required for the activation of two phonons with the same momentum, one backscattering from the other. In our sample, the 2D peak is a single sharp Lorentzian with FWHM(2D) ∼ 26 cm⁻¹, a signature of SLG. Different measurements show similar spectra, indicating uniform quality throughout the sample. The position of the G peak, Pos(G), is ∼ 1588 cm⁻¹, with FWHM(G) ∼ 6 cm⁻¹. The 2D peak position, Pos(2D), is ∼ 2705 cm⁻¹, while the 2D to G peak intensity and area ratios, I(2D)/I(G) and A(2D)/A(G), are ∼ 2.6 and ∼ 5.8, respectively, indicating a p-doping ∼ 300 meV, which corresponds to a carrier concentration ∼ 6 × 10¹² cm⁻².

Another evidence for 1L-MoS₂ comes from the PL spectrum [Figure 4a (green curve)], showing a peak at ∼ 658 nm (∼ 1.88 eV), due to band-to-band radiative recombination in 1L-MoS₂. In order to reveal the underlying PL signature of 1L-MoS₂, we use a point-to-point subtraction between the spectrum of 1L-MoS₂ on PET [Figure 4b (red curve)] and the reference PET spectrum [Figure 4b (black curve)]. Prior to subtraction, the spectra are normalized to the intensity of the Raman peak at ∼ 1615 cm⁻¹ (corresponding to the peak at ∼ 560 nm in Figure 4b), due to the stretching vibrations of benzene rings in PET. As a result, the PL signal of 1L-MoS₂ can be seen in Figure 4a (blue curve) revealing no significant changes after transfer. The subsequent transfer of SLG on 1L-MoS₂ does not alter the 1L-MoS₂ PL position and line shape [Figure 4b (blue curve)].

We then characterize the SLG transferred on 1L-MoS₂/PET. The intense Raman features of the underlying PET substrate [Figure 3c (black curve)] mask the SLG peaks. In order to reveal the Raman signatures of SLG, we first measure the reference spectrum, shown in Figure 3c (black curve), of a PET substrate, using identical conditions as those for SLG/1L-MoS₂/PET. We then implement a point-to-point subtraction, normalized to the intensity of the PET reference spectrum, Figure 3c (black curve), from the total spectrum, Figure 3c (blue curve). The result is in Figure 4a (blue curve).
3b (blue curve). The 2D peak retains its single-Lorentzian line-shape with FWHM(2D) \(\sim 28 \text{ cm}^{-1}\), validating the transfer of SLG. The negligible D peak indicates that no significant defects are induced during transfer. \(\text{Pos}(G) \approx 1583 \text{ cm}^{-1}\), FWHM(G) \(\sim 17 \text{ cm}^{-1}\), Pos(2D) \(\sim 2683 \text{ cm}^{-1}\), and A(2D)/A(G) \(\sim 4.8\), indicating a p-doping \(\sim 4 \times 10^{12} \text{ cm}^{-2}\) \((\sim 250 \text{ meV})\).53,73

We then measure the absorptance and transmittance of SLG/1L-MoS\(_2\) using a broadband (400–1300 nm) white light from a tungsten halogen lamp. The transmitted light is collected by a 10X objective lens (NA = 0.25) with a Horiba Jobin Yvon HR800 spectrometer equipped with a 300 grooves/mm grating, charged coupled device (CCD) detector and a 50 \(\mu\)m pinhole. Figure 5a plots the optical transmittance of bare PET (AbsHetero, blue line), and the final SLG/1L-MoS\(_2\) stack on PET (T\(_{\text{Hetero}}\) blue line) measured in the 400–800 nm wavelength range. Figure 5b plots the absorptance of 1L-MoS\(_2\) on PET (AbsMoS\(_2\), red line) and of SLG/1L-MoS\(_2\) on PET (Abs\(_{\text{MoS}2}\) blue line), calculated as  \(\text{Abs}_\text{MoS}_2 = (T_{\text{PET}} - T_{\text{MoS}_2})/T_{\text{PET}}\) and  \(\text{Abs}_{\text{Hetero}} = (T_{\text{PET}} - T_{\text{Hetero}})/T_{\text{PET}}\). The three peaks in Figure 5b at \(\sim 650 \text{ nm (1.91 eV)}\), \(\sim 603 \text{ nm (2.06 eV)}\) and \(\sim 428 \text{ nm (2.90 eV)}\) correspond to the A, B, C excitons of 1L-MoS\(_2\).75,78 Their positions remain unchanged after SLG transfer. The absorptance difference between the two curves (red and blue) is \(\sim 2.6\%\), consistent with the additional SLG absorption.79

The PD area is shaped by etching, whereby SLG extending beyond the 1L-MoS\(_2\) flake is removed in an oxygen plasma. The source, drain and gate electrodes are then defined by patterning the contacts area, followed by Cr/Au (6 nm/60 nm) evaporation and lift-off. PDs with different channel lengths (100 \(\mu\)m to 1 mm), 2 mm channel width, and common side-gate electrodes (1 \(\times\) 0.5 cm) are built (Figure 1b).

Ref 48 showed that the responsivity of SLG/MoS\(_2\) PDs can be enhanced by gating. This induces a stronger electric field at the SLG/MoS\(_2\) interface and promotes charge transfer. Various gating techniques have been exploited for GRM-based devices, including conventional Si/SiO\(_2\) back-gates,80 high-k dielectrics (Al\(_2\)O\(_3\), HfO\(_2\)),81 chemical dopants,82 ionic liquids,83 and PEs.53,74 In order to gate our SLG/1L-MoS\(_2\) on PET, we employ the latter due to its compatibility with flexible PET (T\(_{\text{PET}}\) black line), 1L-MoS\(_2\) on PET (T\(_{\text{MoS}_2}\), red line), and the final SLG/1L-MoS\(_2\) stack on PET (T\(_{\text{Hetero}}\) blue line) measured in the 400–800 nm wavelength range. Figure 5b plots the absorptance of 1L-MoS\(_2\) on PET (AbsMoS\(_2\), red line) and of SLG/1L-MoS\(_2\) on PET (Abs\(_{\text{MoS}2}\) blue line), calculated as  \(\text{Abs}_\text{MoS}_2 = (T_{\text{PET}} - T_{\text{MoS}_2})/T_{\text{PET}}\) and  \(\text{Abs}_{\text{Hetero}} = (T_{\text{PET}} - T_{\text{Hetero}})/T_{\text{PET}}\). The three peaks in Figure 5b at \(\sim 650 \text{ nm (1.91 eV)}\), \(\sim 603 \text{ nm (2.06 eV)}\) and \(\sim 428 \text{ nm (2.90 eV)}\) correspond to the A, B, C excitons of 1L-MoS\(_2\).75,78 Their positions remain unchanged after SLG transfer. The absorptance difference between the two curves (red and blue) is \(\sim 2.6\%\), consistent with the additional SLG absorption.79

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We then characterize the responsivity at 642 nm (\(\sim 1.93 \text{ eV}\)), slightly above the A exciton peak, where absorption of 1L-MoS\(_2\) is maximized (Figure 5b). At 642 nm the SLG/1L-MoS\(_2\) heterostructure shows \(\sim 8\%\) absorptance (Figure 5b), and the device retains \(\sim 82\%\) transparency (Figure 5a).

The \(I_{DS} - V_{GS}\) measurements in Figure 6a are done at room temperature using a probe station and a parameter analyzer (Keithley 4200). The PD is illuminated at normal incidence by a collimated laser with \(P_o\) ranging from 100 \(\mu\)W to 4 mW. At these \(P_o\) and with \(V_{DS} = 0.1 \text{ V}\) we measure a positive \(V_{ON}\) ranging from \(\sim 0.39\) to 0.47 V, indicating an initial SLG p-doping \(\sim 220 \text{ meV}\), consistent with the Raman estimate.

Figure 6a shows that for \(\sim 1 \text{ V} < V_{GS} < 0.5 \text{ V}\), where SLG transport is hole dominated, the current decreases under illumination (\(\sim 10 \mu\text{A} \text{ at } V_{GS} = -1 \text{ V}\)), as anticipated from the band-diagram of Figure 2. For \(V_{GS} > 0.5 \text{ V}\), where SLG is electron-doped, the PD shows a small (up to \(\sim 0.2\mu\text{A}\)) current increase under illumination. Figure 6b plots \(R_{ext}\) as a function of \(V_{GS}\), as derived from transconductance measurements using:19

\[
R_{ext} = \frac{I_{light} - I_{dark}}{P_o \cdot A_{PD}/A_o} 
\]

(1)

where \(I_{light}\) and \(I_{dark}\) are the PD current under illumination and in dark, \(I_{light} - I_{dark} = I_{ph}\) is the photocurrent defined as the absolute change in the device current upon illumination, \(A_o\) is the laser spot area, \(A_{PD}\) is the PD area, and \(A_{PD}/A_o\) is a scaling factor that takes into account the fact that only a fraction of optical power impinges on the PD. As expected from the band-diagram in Figure 2, \(R_{ext}\) tends to increase for more negative \(V_{GS}\), up to \(\sim 5.5 \text{ A/W} \text{ at } V_{GS} = -1 \text{ V}, V_{DS} = 0.1 \text{ V}\) for \(P_o = 100 \mu\text{W}\). By taking into account that only \(8\%\) of light is absorbed
(\(P_{\text{ph}} = 0.8 \times P_i\)), we derive \(R_{\text{sat}} = R_{\text{sat}}/0.08 = 69\Omega/W\). Figure 6b implies that the higher \(P_{\text{ph}}\), the lower \(R_{\text{sat}}\). This can be explained considering that the more photogenerated electrons are injected into the p-doped channel, the lower the electric field at the SLG/1L-MoS\(_2\) interface, therefore a reduced injection of electrons causes \(R_{\text{sat}}\) to decrease.

Given that \(R_{\text{sat}}R_{\text{sat}} > 1/A/W\), we expect a photoconductive gain (\(G_{\text{PD}}\)), whereby absorption of one photon results in multiple charge carriers contributing to \(I_{\text{ph}}\). Our PDs act as optically gated photodetectors, where the SLG conductance is modulated by optical absorption in the 1L-MoS\(_2\). In this configuration, the presence of \(G_{\text{PD}}\) implies that the injected electrons in SLG can recirculate multiple times between source and drain, before recombining with trapped holes in 1L-MoS\(_2\). Consequently, \(G_{\text{PD}}\) can be estimated as the ratio of electrons recombination (\(t_{\text{rec}}\)) and transit (\(t_{\text{tr}}\)) times in the SLG channel: \(G_{\text{PD}} = t_{\text{rec}}/t_{\text{tr}}\). For higher \(V_{\text{DS}}\), the free carrier drift velocity \(v_d\) in the SLG channel increases linearly with bias (ohmic region) until it saturates, because of carriers scattering with optical phonons. For higher \(V_{\text{DS}}\), \(G_{\text{PD}}\) is also expected to grow linearly with \(V_{\text{DS}}\) providing higher \(R_{\text{sat}}\). To confirm the photoconductive nature of \(G_{\text{PD}}\) in our devices and test the dependence of \(R_{\text{sat}}\) on \(V_{\text{DS}}\) we measure \(I_{\text{DS}}-V_{\text{DS}}\) under illumination at \(P_{\text{ph}} = 100 \mu W\) for \(V_{\text{GS}} = -1\) V and calculate \(R_{\text{sat}}\) using eq 1. The \(I_{\text{DS}}-V_{\text{DS}}\) characteristics of the PD show linear dependence, confirming ohmic behavior of the metal-SLG-metal channel. We use \(V_{\text{DS}} < 1\) V to keep the device operation in the (ohmic) regime and minimize the effects of the nonlinear dependence of \(v_d\) on \(V_{\text{DS}}\) (such as velocity saturation) that might appear for \(V_{\text{DS}} > 1\) V. As shown in Figure 7, \(R_{\text{sat}}\) scales with \(V_{\text{DS}}\) and reaches \(\sim 45.5A/W\) (\(R_{\text{sat}} \sim 570\Omega/A/W\)) at \(V_{\text{DS}} = 1\) V. This is almost 1 order of magnitude higher than at \(0.1\) V, consistent with the similar increase in \(V_{\text{DS}}\). These results are at least 2 orders of magnitude higher than semiconductor flexible membranes. Furthermore, such a combination of high responsivity with \(\mu A\) range photocurrent surpasses that found in other GRM-based PDs in the visible range.

We also fabricate a control device with a 1L-MoS\(_2\) channel only, without SLG. This has \(R_{\text{sat}} \sim 2\) mA/W, which is 4 orders of magnitude smaller than that of our SLG/1L-MoS\(_2\) heterostructure. We thus conclude that SLG/1L-MoS\(_2\) heterostructures are necessary to achieve high (hundreds A/W) responsivity, due to the presence of photoconductive gain.

To assess the photoresponse uniformity in our SLG/1L-MoS\(_2\) heterostructures, we perform photocurrent mapping using the same laser source (642 nm) as for optoelectronic characterizations. We scan areas of \(80 \times 140 \mu m\) (pixel size 3 \(\times\) 3 \(\mu m\)) at different locations. At each position (pixel) the device photocurrent is measured for \(V_{\text{DS}} = 0.3\) V (Figure 8a). We also collect the backscattered light to give reflection map (Figure 8b). Figure 8a indicates that the entire channel area confined between the source-drain electrodes is photoactive, and shows uniform photocurrent photosresponse with standard deviation \(\pm 15\%\). We thus conclude that interface imperfections (e.g., bubbles, polymer residuals, etc.) have minor effect on the charge transfer process from MoS\(_2\) to graphene. We define \(G_{\text{PD}}\) as the ratio between electrons recirculating in the SLG channel, thus sustaining \(I_{\text{ph}}\), and the initial electron concentration injected into SLG from 1L-MoS\(_2\): \(\Delta n_{\text{ch}}\),

\[
G_{\text{PD}} = \frac{q}{\text{APD}} \Delta n_{\text{ch}}
\]

where \(q\) is the electron charge and \(\Delta n_{\text{ch}}\) is the concentration per unit area and per unit time of the injected electrons. \(\Delta n_{\text{ch}}\) is equal to the trapped-hole concentration per unit area and per unit time in 1L-MoS\(_2\), which is related to a charge neutrality point shift \(\Delta V_{\text{GS}} = \Delta V_{\text{CNP}}\) in the transfer characteristics. To calculate \(\Delta n_{\text{ch}}\) we first write the potential balance in the metal-dielectric-SLG structure. When \(V_{\text{GS}}\) is applied, it creates a gate-to-channel potential drop \(V_{\text{dieled}}\), and it induces a local electrostatic potential in the graphene channel \(V_{\text{ch}} = E_\text{p}/\text{q}\):

\[
V_{\text{GS}} = V_{\text{dieled}} + V_{\text{ch}} = \frac{Q_G}{C_G} + V_{\text{ch}}
\]

where \(Q_G\) and \(C_G\) are the charge concentration and the geometrical capacitance per unit area associated with the gate electrode, respectively. \(Q_G = q \tau_{\text{n}_{\text{ch}}},\) reflecting the charge neutrality of the gate capacitor, with \(\tau_{\text{n}_{\text{ch}}}\) the charge carrier concentration per unit area in the channel induced by \(V_{\text{GS}}\). Any variations of \(\tau_{\text{n}_{\text{ch}}}\) change \(Q_G\) and \(V_{\text{GS}}\). From eq 3 we get:

\[
\frac{dV_{\text{GS}}}{dQ_G} = \frac{1}{C_G} + \frac{dV_{\text{ch}}}{dQ_G}
\]

which leads to

\[
\Delta Q_G = (1/C_G + 1/C_Q)^{-1} \Delta V_{\text{GS}}
\]

where \(C_Q = dQ_G/dV_{\text{ch}}\) is the SLG quantum capacitance, which characterizes the changes of the channel potential \(V_{\text{ch}}\) as a result of additional gating \(\Delta Q_G\) and \((1/C_G + 1/C_Q)^{-1}\) is the total capacitance \(C_{\text{tot}}\).

To calculate \(Q_G\) and \(\Delta n_{\text{ch}}\) we first need to find \(C_G\) and \(C_Q\). In PE gating, \(C_G\) is associated with the electric double layer (EDL) at the SLG/electrolyte interface. The EDL acts like a parallel-plate capacitor with a dielectric layer thickness of the order of the Debye length \(\lambda_D\) so that \(C_G = C_{\text{EDL}} = \varepsilon_\varepsilon_0/\lambda_D\), where \(\varepsilon\) is the PE dielectric constant, and \(\varepsilon_0\) is the vacuum permittivity. In principle, for a monovalent electrolyte, \(\lambda_D\) can be explicitly calculated if the electrolyte concentration is known. However, in the presence of a polymer matrix, the electrolyte ions can form complexes with polymer chains, therefore the precise ion concentration is difficult to measure. For PE gating, different EDL thicknesses in the range \(\sim 1-5\) nm have been reported. To estimate \(C_{\text{EDL}}\) in our devices,

![Figure 7. \(R_{\text{sat}}\) as a function of \(V_{\text{DS}}\) for \(P_i = 100\) \(\mu W\) at \(V_{\text{GS}} = -1\) V.](image-url)
we take $\lambda_0 \sim 2$ nm$^{53}$ and the dielectric constant of the poly(ethylene oxide) matrix to be $\epsilon \sim 5^{96}$ as done in ref $^{53}$. As a result, we obtain $C_{EDL} = 2.2 \times 10^{-6}$ F/cm$^2$. This is the same order of magnitude as the SLG $C_Q^{90}$. Therefore, the latter cannot be neglected in eq 5. $C_Q$ is given by$^{90}$

$$C_Q \approx \frac{2q^2}{\hbar v_F \sqrt{n_i + n_i}},$$

(6)

where $\hbar$ is the reduced Planck constant, $v_F = 1.1 \times 10^6$ m/s is the SLG Fermi velocity,$^{80,97}$ and $n_i$ is the intrinsic carrier concentration in SLG near the Dirac point induced by charge impurities, defects and local potential fluctuations in the SLG channel.$^{90,98}$ From our Raman and transconductance measurements we estimate $n_i \sim 3 \times 10^{12}$ cm$^{-2}$. From eq 6 we then get $C_Q \approx 4 \times 10^{-6}$ F/cm$^2$ at $V_{CNP}$. From Figure 6a, and extracting $\Delta V_{CNP}$ between the dark current and the transfer curves measured under illumination, and with eq 5, we get $\Delta n_{ch}$ ranging from 4 to $8 \times 10^{11}$ cm$^{-2}$ for $P_o$ going from 100 $\mu$W to 4 mW. As a result, we obtain $G_{PD} \sim 5 \times 10^4$ at $V_{DS} = 0.1$ V for different $P_o$, as shown in Figure 9. As discussed previously, $G_{PD}$ becomes larger for higher $V_{DS}$. Thus, we measure an increase of almost 1 order of magnitude ($G_{PD} \sim 4 \times 10^5$ at $P_o = 100$ $\mu$W) for $V_{DS}$ going from 0.1 to 1 V.

Finally, we test $I_{ph}$ as a function of bending using a Deben Microtest three-point bending setup (Figure 10a). In this case, $r_b = \sqrt{h^2 + (L/2)^2}/h$, where $L$ is the chord of circumference connecting the two ends of the arc, and $h$ is the height at the chord midpoint. The plotted values of $I_{ph}$ in the bent state at each $r_b$ ($I_{ph,bend}$) are normalized to the values of $I_{ph}$ measured at rest with the sample in the flat position ($I_{ph,rest}$). Figure 10b plots the normalized $I_{ph,bend}/I_{ph,rest}$ for different $r_b$, showing

**Figure 8.** (a) Photocurrent map of channel area, simultaneously measured with backscattered light map. A uniform signal is observed in the channel area (between the electrodes). (b) Reflection map of backscattered light from the device channel. The yellow areas, corresponding to the contact areas, show higher reflectance than the substrate (in blue).

**Figure 9.** $G_{PD}$ as a function of $P_o$ at $V_{GS} = -1$ V and $V_{DS} = 0.1$ V.

**Figure 10.** (a) Schematic three-point bending setup. LD = laser diode; FC= fiber collimator; (b) $I_{ph,bend}$ normalized to the value at rest $I_{ph,rest}$ as a function of $r_b$; (c) $I_{ph,bend}$ normalized to the value at rest $I_{ph,rest}$ as a function of the number of bending cycles.
deviations within 15% for \( r_b \) down to 1.4 cm. This \( r_b \) is comparable to that reported for semiconductor membrane PDs, yet the latter have 2 orders of magnitude lower (<0.3 A/W) responsivities. Although our \( r_b \) is five times larger than that reported for flexible single NW devices, the area of our PDs (>40 mm\(^2\)) is at least 6 orders of magnitude larger than that of the NW devices (<5 \( \mu \)m\(^2\)). To test the device performance upon bending cycles, we first measure the photocurrent at rest (\( I_{\text{photost}} \) flat position) and then at the smallest \( r_b \) (\( I_{\text{ph, bend}} \sim 1.4 \) cm), repeating these measurements for 30 bending cycles. Figure 10c plots \( I_{\text{ph, bend}}/I_{\text{photost}} \) as a function of bending cycles. This shows that our PDs retain stable photocurrent after multiple bending tests with a \( I_{\text{ph, bend}}/I_{\text{photost}} \) standard deviation ±12%.

CONCLUSIONS

We reported polymer electrolyte gated, flexible photodetectors, for visible wavelengths with external responsivity up to ~43.5 A/W, photocooperative gain ~4 \( \times \) 10\(^5\), operation voltage <1 V, and optical transparency >82%. The responsivity is at least 2 orders of magnitude higher than in semiconductor flexible membranes. The device shows stable performance upon bending for radii of curvature larger than ~1.4 cm. Owing to their responsivity, flexibility, transparency, and low operation voltage, our photodetectors can be attractive for wearable, biomedical, and low-power optoelectronic applications.

METHODS

1L-MoS\(_2\) is epitaxially grown by CVD on c-plane sapphire substrates. These are annealed at 1000 °C in air for 1 h after successive cleaning by acetone/isopropyl alcohol/DI water. They are then placed face-down above a crucible containing ∼5 mg MoO\(_3\) (≥99.998% purity, Sigma-Aldrich) is located upstream from 5 mg sulfur (≥99.99% purity, Sigma-Aldrich) is located upstream from a 32 mm outer diameter quartz tube placed down above a crucible containing ∼700 °C for 10 min, cool to 570 °C for 10 min, cool to 570 °C with 10 sccm Ar, increase the gas flow, set at 100 sccm Ar flow, and open the furnace for rapid cooling. SLG is grown on a 35 mm sulfur (≥99.998% purity, Sigma-Aldrich) is located upstream from 5 mg sulfur (≥99.998% purity, Sigma-Aldrich) is located upstream from a 32 mm outer diameter quartz tube placed down above a crucible containing ∼700 °C for 10 min, cool to 570 °C with 10 sccm Ar, increase the gas flow, set at 100 sccm Ar flow, and open the furnace for rapid cooling. SLG is grown on a 35 \( \mu \)m Cu foil, following the process described in ref 51. The sample is then cooled in vacuum (1 mTorr) to room temperature and removed from the chamber.

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Notes
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REFERENCES

(1) Akinwande, D.; Petrone, N.; Hone, J. Two-Dimensional Flexible Nanoelectronics. Nat. Commun. 2014, 5, 5678.
(2) Ryhänen, T. Nanotechnologies for Future Mobile Devices; Cambridge University Press: Cambridge, U.K., 2010.
(3) Liu, Z.; Chen, G.; Liang, B.; Yu, G.; Huang, H.; Chen, D.; Shen, G. Fabrication of High-Quality ZnTe Nanowires Toward High-Performance Rigid/Flexible Visible-Light Photodetectors. Opt. Express 2013, 21, 7799–7810.
(4) Yuan, H.-C.; Shin, J.; Qin, G.; Sun, L.; Bhattacharya, P.; Lagally, M. G.; Celler, G. K.; Ma, Z. Flexible Photodetectors on Plastic Substrates By Use of Printing Transferred Single-Crystal Germanium Membranes. Appl. Phys. Lett. 2009, 94, 013102.
(5) Park, S.-I.; Xiong, Y.; Kim, R.-H.; Elvikis, P.; Meitl, M.; Kim, D.-H.; Wu, J.; Yoon, J.; Yu, C.-J.; Liu, Z.; Huang, Y.; Hwang, K.-C.; Ferreira, P.; Li, X.; Choquette, K.; Rogers, J. A. Printed Assemblies of Inorganic Light-Emitting Diodes for Deformable and Semitransparent Displays. Science 2009, 325, 977–981.
(6) Qiang, Z.; Yang, H.; Chen, L.; Pang, H.; Ma, Z.; Zhou, W. Fano Filters Based on Transferred Silicon Nanomembranes on Plastic Substrates. Appl. Phys. Lett. 2008, 93, 061106.
(7) Bosman, E.; Van Steenberge, G.; Van Hoe, B.; Missinne, J.; Vanfleteren, J.; Van Daele, P. Highly Reliable Flexible Active Optical Links. IEEE Photonics Technol. Lett. 2010, 22, 287–289.
(8) Chen, Z.; Ren, W.; Gao, L.; Liu, B.; Pei, S.; Cheng, H.-M. Three-Dimensional Flexible and Conductive Interconnected Graphene Networks Grown by Chemical Vapor Deposition. Nat. Mater. 2011, 10, 424–428.
(9) Shahi, S. Photovoltaics: Flexible Optoelectronics. Nat. Photonics 2010, 4, 506.
(10) Yoon, J.; Li, L.; Semichaevsky, A. V.; Ryu, J. H.; Johnson, H. T.; Nuzzo, R. G.; Rogers, J. A. Flexible Concentrator Photovoltaics Based on Microscale Cellophane Solar Cells Embedded in Luminescent Waveguides. Nat. Commun. 2011, 2, 343.
(11) Kim, D.-H.; Lu, N.; Ma, R.; Kim, Y.-S.; Kim, R.-H.; Wang, S.; Wu, J.; Won, S. M.; Tao, H.; Islam, A.; Yu, K. J.; Kim, T.-I.; Chowdhury, R.; Ying, M.; Xu, L.; Li, M.; Chung, H.-J.; Keum, H.; McCormick, M.; Liu, P.; et al. Epidermal Electronics. Science 2011, 333, 838–843.
(12) Ko, H. C.; Stoykovich, M. P.; Song, J.; Malarchuk, V.; Choi, W. M.; Yu, C.-J.; Geddes, J. B.; Illi, Xiao; J.; Wang, S.; Huang, Y.; Rogers, J. A. A Hemispherical Electronic Eye Camera Based on Compressible Silicon Photodetectors. Nature 2008, 454, 748–753.
(13) Blakemore, J. S. Flexible and Organic LEDs. Mater. Today 2012, 1277–1278.
(14) MacMillan, N. H. The Theoretical Strength of Solids. J. Mater. Sci. 1972, 7, 239–254.
(15) Yang, W.; Yang, H.; Qin, G.; Ma, Z.; Berggren, J.; Hammar, M.; Soref, R.; Zhou, W. Large-Area InP-Based Crystalline Nanomembrane Flexible Photodetectors. Appl. Phys. Lett. 2010, 96, 121107.
(16) Chen, G.; Liang, B.; Liu, Z.; Yu, G.; Xie, X.; Luo, T.; Xie, Z.; Chen, D.; Zhu, M.-Q.; Shen, G. High Performance Rigid and Flexible Visible-Light Photodetectors Based on Aligned X(110), GaP Nanowire Arrays. J. Mater. Chem. C 2014, 2, 1270–1277.
(17) Lee, S.; Jung, S. W.; Park, S.; Ahn, J.; Hong, S. J.; Yoo, H. J.; Lee, M. H.; Cho, D. I. Ultra-High Responsivity, Silicon Nanowire Photodetectors for Retinal Prosthesis. In IEEE MEMS 25th International Conference, Paris, France, January 29–February 2, 2012; IEEE: New York; pp 1364–1367.
(18) Yu, G.; Liu, Z.; Xie, X.; Ouyang, X.; Shen, G. Flexible Photodetectors with Single-Crystalline GaTe Nanowires. J. Phys. Chem. C 2014, 2, 6104–6110.
(19) Zee, S. M.; Kwock, K. C. Physics of Semiconductor Devices; Wiley: New York, 2006.
(20) Bonaccorso, F.; Sun, Z.; Hasan, T.; Ferrari, A. C. Graphene Photonics and Optoelectronics. Nat. Photonics 2010, 4, 611–622.
(21) Ferrari, A. C.; Bonaccorso, F.; Fal’ko, V.; Novoselov, K. S.; Roche, S.; Boggild, P.; Borini, S.; Koppens, F. H. L.; Palermo, L.; Pugno, N.; Garrido, J. A.; Sordan, R.; Bianco, A.; Ballerini, L.; Prato,
Graphene.

Heterojunction.

(22) Koppens, F. H. L.; Mueller, T.; Avouris, P.; Ferrari, A. C.; Vitiello, M. S.; Polini, M. Photodetectors Based on Graphene, Other Two-Dimensional Materials and Hybrid Systems. Nat. Nanotechnol. 2011, 6, 781–788.

(23) Sun, Z. P.; Hasan, T.; Torrisi, F.; Popa, D.; Privitera, G.; Wang, F. Q.; Bonaccorso, F.; Basko, D. M.; Ferrari, A. C. Graphene Mode-Locked Ultrafast Laser. ACS Nano 2010, 4, 803–810.

(24) Kim, K. S.; Zhao, Y.; Jang, H.; Lee, S. Y.; Kim, J. M.; Kim, K. S.; Ahn, J.-H.; Kim, P.; Choi, J.-Y.; Hong, B. H. Large-Scale Pattern Growth of Graphene Films for Stretchable Transparent Electrodes. Nature 2009, 457, 706–710.

(25) Baugher, B. W. H.; Churchill, H. O. H.; Yang, Y.; Jarillo-Herrero, P. Optoelectronic Devices Based on Electrically Tunable p-n Diodes in a Monolayer Dichalcogenide. Nat. Nanotechnol. 2014, 9, 262–267.

(26) Pospischil, A.; Furchi, M. M.; Mueller, T. Solar-Energy Conversion and Light Emission in an Atomic Monolayer p-n Diode. Nat. Nanotechnol. 2014, 9, 257–261.

(27) Lopez-Sanchez, O.; Lembde, D.; Kayci, M.; Radenovic, A.; Kis, A. Ultrasensitive Photodetectors Based on Monolayer MoS 2 . Nat. Nanotechnol. 2013, 8, 497–501.

(28) Xia, F. N.; Mueller, T.; Lin, Y. M.; Valdes-Garcia, A.; Avouris, P. Ultrafast Graphene Photodetector. Nat. Nanotechnol. 2009, 4, 839–843.

(29) Mueller, T.; Xia, F. N. A.; Avouris, P. Graphene Photodetectors for High-Speed Optical Communications. Nat. Photonics 2010, 4, 297–301.

(30) Liu, M.; Yin, X. B.; Ulin-Avila, E.; Geng, B. S.; Zentgraf, T.; Ju, L.; Wang, F.; Zhang, X. A Graphene-Based Broadband Optical Modulator. Nature 2011, 474, 64–67.

(31) Chen, J.; Badioli, M.; Alonso-Gonzalez, P.; Thongrattanasiri, S.; Huth, F.; Osmond, J.; Spasenovic, M.; Centeno, A.; Pesquera, A.; Godignon, P.; Zarutuza Elorza, A.; Camara, N.; de Abajo, F. J. G.; Hillenbrand, R.; Koppens, F. H. L. Optical Nano-Imaging of Gate-Tunable Graphene Plasmons. Nature 2012, 487, 77–81.

(32) Echtermeyer, T. J.; Britnell, L.; Jasnos, P. K.; Lombardo, A.; Gorbachev, R. V.; Grigorenko, A. N.; Geim, A. K.; Ferrari, A. C.; Novoselov, K. S. Strong Plasmonic Enhancement of Photovoltaic Conversion in Graphene. Nat. Commun. 2011, 2, 458.

(33) Fei, Z.; Rodin, A. S.; Andreev, G. O.; Bao, W.; McLeod, A. S.; Wagner, M.; Zhang, L. M.; Zhao, Z.; Thiemens, M.; Dominguez, G.; Fogler, M. M.; Neto, A. H. C.; Lau, C. N.; Keilmann, F.; Basov, D. N. Gate-Tuning of Graphene Plasmons Revealed by Infrared Nano-Imaging. Nature 2012, 487, 82–85.

(34) Ja, L.; Geng, B.; Hong, J.; Girit, C.; Martin, M.; Hao, Z.; Bechtel, H. A.; Liang, X.; Zettl, A.; Shen, Y. R.; Wang, F. Graphene Plasmonics for Tunable Terahertz Metamaterials. Nat. Nanotechnol. 2011, 6, 630–634.

(35) Yan, H.; Li, X.; Chandra, B.; Tulevski, G.; Wu, Y.; Freitag, M.; Zhu, W.; Avouris, P.; Xia, F. Tunable Infrared Plasmonic Devices Using Graphene/Insulator Stacks. Nat. Nanotechnol. 2012, 7, 330–334.

(36) Furchi, M. M.; Pospischil, A.; Libisch, F.; Burgdörfer, J.; Mueller, T. Photovoltaic Effect in an Electrically Tunable Van der Waals Heterojunction. Nano Lett. 2014, 14, 4785–4791.

(37) Withers, F.; Del Pozo-Zamudio, O.; Mishchenko, A.; Rooney, A. P.; Gholinia, A.; Watanabe, K.; Taniguchi, T.; Haigh, S. J.; Geim, A. K.; Tödtlowiski, A. J.; Novoselov, K. S. Light-Emitting Diodes by Backgate Structure Engineering in Van der Waals Heterostructures. Nat. Mater. 2015, 14, 301–306.

(38) Hu, P. A.; Wang, L. F.; Yoon, M.; Zhang, J.; Feng, W.; Wang, X. N.; Wen, Z. I.; Idrobo, J. C.; Miyamoto, Y.; Gehegan, D. B.; Xiao, K. Highly Responsive Ultrathin GaS Nanosheet Photodetectors on Rigid and Flexible Substrates. Nano Lett. 2013, 13, 1649–1654.

(39) Hsiao, Y.-J.; Fang, T.-H.; Ji, L.-W.; Yang, B.-Y. Red-Shift Effect and Sensitive Responsivity of MoS 2 /ZnO Flexible Photodetectors. Nanoscale Res. Lett. 2015, 10, 443.
(56) Das, S.; Chen, H.-Y.; Penumatcha, A. V.; Appenzeller, J. High Performance Multilayer MoS2 Transistors with Scandium Contacts. Nano Lett. 2013, 13, 100–105.
(57) Shan, B.; Cho, K. First Principles Study of Work Functions of Single Wall Carbon Nanotubes. Phys. Rev. Lett. 2005, 94, 236602.
(58) Yu, T.-J.; Zhao, Y.; Ryu, S.; Brus, L. E.; Kim, K. S.; Kim, P. Tuning the Graphene Work Function by Electric Field Effect. Nano Lett. 2009, 9, 5432–5434.
(59) Kim, B. J.; Jang, H.; Lee, S.-K.; Hong, B. H.; Ahn, J.-H.; Cho, J. H. High Performance Flexible Graphene Field Effect Transistors with Ion Gel Gate Dielectrics. Nano Lett. 2010, 10, 3464–3466.
(60) Lee, S. K.; Jang, H. Y.; Jang, S.; Choi, E.; Hong, B. H.; Lee, J.; Park, S.; Ahn, J. H. All Graphene-Based Thin Film Transistors on Flexible Plastic Substrates. Nano Lett. 2012, 12, 3472–3476.
(61) Dumencu, D.; Ovchininkov, D.; Marinov, K.; Lazić, P.; Gibertini, M.; Marzari, N.; Sanchez, O. L.; Kung, Y.-C.; Rasanohon, D.; Chen, M.-W.; Bertolazzi, S.; Gillet, P. Large-Area Epitaxial Monolayer MoS2. ACS Nano 2015, 9, 4611–4620.
(62) Li, X. S.; Cai, W. W.; An, J. H.; Kim, S.; Nah, J.; Yang, D. X.; Piner, R.; Velamakanni, A.; Jung, I.; Tutuc, E.; Banerjee, S. K.; Colombo, L.; Ruoff, R. S. Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. Science 2009, 324, 1312–1314.
(63) Verbie, J. L.; Wieting, T. J. Lattice Mode Degeneracy in MoS2 and Other Layer Compounds. Phys. Rev. Lett. 1970, 25, 362–365.
(64) Wieting, T. J.; Verbie, J. L. Infrared and Raman Studies of Long-Wavelength Optical Phonons in Hexagonal MoS2. Phys. Rev. B 1971, 3, 4286–4292.
(65) Lee, C.; Yan, H. G.; Brus, L. E.; Heinz, T. F.; Hone, J.; Ryu, S. Anomalous Lattice Vibrations of Single- and Few-Layer MoS2. ACS Nano 2010, 4, 2695–2700.
(66) Li, H.; Zhang, Q.; Yap, C. C. R.; Tay, B. K.; Geim, A. K. Raman Spectrum of Graphene and Graphene Layers. Phys. Rev. B: Condens. Matter Mater. Phys. 2009, 80, 153432–153441.
(67) Cançado, L. G.; Jorio, A.; Ferreira, E. H. H.; Stavole, F.; Achete, C. A.; Capaz, R. B.; Moutinho, M. V.; Lombardo, A.; Kalim, T. S.; Ferrari, A. C. Quantifying Defects in Graphene Via Raman Spectroscopy at Different Excitation Energies. Nano Lett. 2011, 11, 3190–3196.
(68) Ferrari, A. C.; Robertson, J. Interpretation of Raman Spectra of Disordered and Amorphous Carbon. Phys. Rev. B: Condens. Matter Mater. Phys. 2000, 61, 14095–14107.
(69) Basko, D. K.; Efetov, D. K.; Kim, P. Controlling Electron-Phonon Interactions in Graphene at Ultrahigh Carrier Densities. Phys. Rev. Lett. 2010, 105, 256805.
(70) Konstantatos, G.; Badioli, M.; Gaudreau, L.; Osmond, J.; Bennechea, M.; Garcia de Arquer, F. P.; Gatti, F.; Koppens, F. H. Hybrid Graphene-Quantum Dot Phototransistors with Ultrahigh Gain. Nat. Nanotechnol. 2012, 7, 363–368.
(71) Meric, I.; Han, M. Y.; Young, A. F.; Ozyilmaz, B.; Kim, P.; Shepard, K. L. Current Saturation in Zero-Bandgap, Top-Gated Graphene Field-Effect Transistors. Nat. Nanotechnol. 2008, 3, 654–659.
(72) Robinson, J. A.; LaBella, M.; Zhu, M.; Hollander, M.; Kasarda, R.; Hughes, Z.; Trombull, K.; Cavalerio, R.; Snyder, D. Contacting Graphene. Appl. Phys. Lett. 2011, 98, 053103.
(73) Xia, J.; Chen, F.; Li, J.; T. J.; Tao, N. Measurement of the Quantum capacitance of Graphene. Nat. Nanotechnol. 2009, 4, 505–509.
(74) Fang, T.; Konar, A.; Xing, H. Z.; Jena, D. Carrier Statistics and Quantum Capacitance of Graphene Sheets and Ribbons. Appl. Phys. Lett. 2007, 91, 092109.
(75) Ozcel, T.; Gaur, A.; Rogers, J. A.; Shim, M. Polymer Electrolyte Gating of Carbon Nanotube Network Transistors. Nano Lett. 2005, 5, 905–911.
(76) Lu, C.; Fu, Q.; Huang, S.; Liu, J. Polymer Electrolyte-Gated Carbon Nanotube Field-Effect Transistor. Nano Lett. 2004, 4, 623–627.
(77) Russel, W. B.; Saville, D. A.; Schowalter, W. R. Colloidal Dispersions; Cambridge University Press: Cambridge, U.K., 1989.
(78) Basko, D. K.; Efetov, D. K.; Kim, P. Experimental Observation of the Quantum Hall Effect and Berry’s Phase in Graphene. Nature 2005, 438, 201–204.
(98) Adam, S.; Hwang, E. H.; Galitski, V. M.; Das Sarma, S. A Self-Consistent Theory for Graphene Transport. Proc. Natl. Acad. Sci. U. S. A. 2007, 104, 18392–18397.

(99) Chen, J. H.; Jang, C.; Adam, S.; Fuhrer, M. S.; Williams, E. D.; Ishigami, M. Charged-Impurity Scattering in Graphene. Nat. Phys. 2008, 4, 377–381.

(100) Galitski, V. M.; Adam, S.; Das Sarma, S. Statistics of Random Voltage Fluctuations and the Low-Density Residual Conductivity of Graphene. Phys. Rev. B: Condens. Matter Mater. Phys. 2007, 76, 245405.