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 centimetre-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 45.5A/W and the internal 570A/W at 642nm. This is at least two orders of magnitude higher than bulk-semiconductor flexible membranes. The photoconductive gain is up to $4 \times 10^5$. The photocurrent is in the 0.1-100µA range. The devices are semi-transparent, with just 8% absorption at 642nm and work stably upon bending to a curvature of 1.4cm. These capabilities and the low voltage operation ($<1V$) make them attractive for wearable applications.

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Modern electronic and opto-electronic systems such as smart phones, smart glasses, smart watches, wearable devices and electronic tattoos increasingly require ultra-thin, transparent, low-cost and energy efficient devices on flexible substrates.\textsuperscript{1} The rising demand for flexible electronics and optoelectronics requires materials which can provide a variety of electrical and optical functionalities, with constant performance upon application of strain.\textsuperscript{2} A wide range of optoelectronic devices on flexible substrates have been reported to date, such as photodetectors (PDs),\textsuperscript{3,4} light emitting diodes (LEDs),\textsuperscript{5} optical filters,\textsuperscript{6} optical interconnects,\textsuperscript{7,8} photovoltaic devices\textsuperscript{9,10} and biomedical sensors.\textsuperscript{11,12}

Major challenges in the development of flexible optoelectronic devices stem from the limitations associated with the high stiffness of bulk semiconductors.\textsuperscript{13,14} In the case of flexible PDs, the current approaches primarily rely on thin (\textmu{}m-thick) semiconductor membranes\textsuperscript{4,15} and compound semiconductor nanowires (NWs),\textsuperscript{3,16–18} mainly because of their ability to absorb light throughout the whole visible range (0.4-0.7\textmu{}m) and the possibility to adapt their fabrication techniques from rigid to plastic, or deformable substrates.\textsuperscript{1}

One of the key parameters for PDs characterization is the responsivity. This is defined as the ratio between the collected photocurrent ($I_{\text{ph}}$) and the optical power. The responsivity is named external ($R_{\text{ext}} = I_{\text{ph}}/P_\text{o}$)\textsuperscript{19} or internal ($R_{\text{int}} = I_{\text{ph}}/P_{\text{abs}}$),\textsuperscript{19} whenever the incident ($P_\text{o}$) or absorbed ($P_{\text{abs}}$) optical power is used at the denominator. Since not all incident photons are absorbed by a PD, i.e. $P_{\text{abs}} < P_\text{in}$, then $R_{\text{int}}$ is typically larger than $R_{\text{ext}}$.\textsuperscript{19}

In flexible PDs, $R_{\text{ext}}$ up to $\sim 0.3$A/W was reported for crystalline semiconductor membranes (InP, Ge)\textsuperscript{4,15} with integrated p-i-n junctions, showing photocurrent up to $\sim 100\mu$A, with $\sim 30\%$ degradation upon bending at a radius $r_b \sim 3$cm.\textsuperscript{15} PDs made of a single semiconductor NW on flexible substrates\textsuperscript{3,16–18} demonstrated $R_{\text{ext}}$ up to $\sim 10^5$A/W, for $r_b$ down to 0.3cm.\textsuperscript{3} Yet, these provide limited $I_{\text{ph}}$ in the order of $n$A\textsuperscript{3,16,18} up to less than $1$\mu{}A.\textsuperscript{17} For flexible devices exploiting NW-arrays by drop-casting,\textsuperscript{3,16,18} rather than based on single-NWs, $R_{\text{ext}}$ degrades significantly from $\sim 10^5$A/W to the mA/W range,\textsuperscript{3,16,18} due to photocurrent loss at multiple junctions in the NW network.\textsuperscript{3,16,18}
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, and ultra-fast lasers. Heterostructures, obtained by stacking layers of different materials were also explored, e.g. in photovoltaic and light emitting devices.

Flexible PDs based on graphene and related materials (GRM) were studied for ultraviolet, visible and near infrared bands. In these devices, different materials and heterostructures produced by mechanical exfoliation, CVD, and liquid phase exfoliation (LPE) were employed. The flexible PDs produced by mechanical exfoliation have a small photoactive area, and they cannot be scaled up to mass production. LPE-based PDs have low responsivity. Ref. showed that thick films of chemically modified and charge-transfer optimized LPE/polymer composites can provide responsivity at near infrared bands. Nevertheless, these PDs require high operation voltage and are non-transparent. Flexible PDs at 450nm using CVD MoS$_2$ transistors and MoS$_2$/WS$_2$ heterostructures were previously reported, and PDs at 780nm were prepared from doped SLG pn-junctions. However, these devices have responsivity in the mA/W range. CVD-based SLG/MoS$_2$ heterostructures showed good photodetection on rigid Si/SiO$_2$ substrates, with back-gate dependent responsivity for optical intensities <0.1pW/µm$^2$.

Here we demonstrate a polymer electrolyte gated, CVD-based flexible PD for visible wavelengths with large photoactive area combined with high responsivity (hundreds A/W), high transparency, gate tunability, low operation voltage and stable (±12%) $I_{ph}$ upon multiple bending cycles with bending radius <1.4cm. The device is assembled by stacking on a PET substrate a centimetre-scale CVD SLG on top of a CVD-grown single layer MoS$_2$ (1L-MoS$_2$). In this configuration, 1L-MoS$_2$ acts as visible light absorber, while SLG is the conductive channel for photocurrent flow. We show that $R_{ext}$ increases either by promoting the carrier injection from 1L-MoS$_2$ to SLG using polymer electrolyte gating, or by increasing the source-drain voltage. This $R_{ext}$ is achieved in devices with ~82% transparency, twice that reported for...
semiconductor membrane devices. We get $R_{int} \sim 570 \text{A/W}$ for $\sim 0.1 \text{nW/µm}^2$ at 642nm, similar to SLG/MoS$_2$ PDs on rigid substrate operating at the same optical power level. This shows that SLG/MoS$_2$ heterostructures on PET retain their photodetection capabilities. Upon bending, our devices have stable performance for $r_b$ down to $\sim 1.4 \text{cm}$. This is comparable to $r_b$ measured in semiconductor membranes PDs, which show lower (< 0.3A/W) responsivities. Although our $r_b$ is one order of magnitude larger than for flexible single NWs, the latter had at least three orders of magnitude smaller device areas (< 5µm$^2$) compared to our PDs (> 0.2mm$^2$). Given the responsivity, flexibility, transparency and low operation voltage (below 1V), our PDs may be integrated in wearable, biomedical and low-power opto-electronic applications.

**Results and discussion**

Fig.1 plots a schematic drawing of our PDs. We fabricated 4 PD arrays with 10 devices each, with channel lengths of 100µm, 200µm, 500µm and 1mm. Each device consists of a 1L-MoS$_2$ 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-MoS$_2$ is used as
absorber in order to preserve a >80% transparency, considered suitable by industry for wearable applications.\textsuperscript{52} The SLG/1L-MoS\textsubscript{2} heterostructure is gated using a polymer electrolyte.\textsuperscript{53,54}

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{schematic_diagram.png}
\caption{Schematic band diagram of polymer electrolyte (PE) gated SLG/1L-MoS\textsubscript{2} PD at a) zero, b) negative and c) positive $V_{GS}$}
\end{figure}

The operation principle of our devices is depicted in Fig.2. For energy bands alignment, the electron affinity of 1L-MoS\textsubscript{2} and the Dirac point of SLG are assumed to be \(\sim 4.4\text{eV}\)\textsuperscript{55,56} and \(\sim 4.6\text{eV}\),\textsuperscript{57,58} respectively. We also assume SLG to be initially p-doped (Fig.2a), as reported in previous works involving SLG transferred on PET.\textsuperscript{59,60} At zero voltage the device is in thermodynamic equilibrium with a constant Fermi level ($E_F$) across the structure and zero current flow between the layers. SLG is initially p-doped (Fig.2a), so that $E_F$ is initially located below the Dirac point. During illumination and photon absorption in MoS\textsubscript{2}, part of the photo-generated electrons would be injected from the 1L-MoS\textsubscript{2} conduction band into the lower energy states in p-doped SLG,\textsuperscript{48} leaving behind the uncompensated charge of photogenerated holes. The latter would be trapped in 1L-MoS\textsubscript{2} and act as an additional positive $V_{GS}$ to the SLG channel, seen as a shift of the charge neutrality point ($V_{CNP}$) to more negative voltages. In p-doped SLG, the injected electrons from 1L-MoS\textsubscript{2} would occupy energy states above $E_F$ (Fig.2b), thus reducing the holes concentration and decreasing the holes current in the SLG channel. Electron injection can be further promoted by gating. When 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} (Fig.2b). Hence, for negative $V_{GS}$, $R_{ext}$ is expected to increase, due to injection of more photo-electrons to SLG and consequent more pronounced PD 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 $E_F$ towards the Dirac point. In this case, the photogenerated electrons in 1L-MoS$_2$ would experience weaker electric fields at the SLG/1L-MoS$_2$ interface, and would become less attracted by the SLG channel. Thus, we expect $R_{ext}$ to decrease. For high enough positive $V_{GS}$, $E_F$ crosses the Dirac point, and SLG becomes n-doped (Fig.2c). As a result, only a weak electron injection from 1L-MoS$_2$ would be possible, if $E_F$ in SLG remains below the 1L-MoS$_2$ conduction band, retaining a weak electric field at the interface. In this regime, the transferred electrons increase the free carrier concentration in the n-doped channel, hence only minor increments of $R_{ext}$ and $I_{ph}$ are expected.

Our devices are built as follows. 1L-MoS$_2$ is epitaxially grown by CVD on c-plane sapphire substrates. These are annealed at 1000°C in air for 1 hour after consecutive cleaning by acetone/isopropyl alcohol/deionized (DI) water. They are then placed face-down above a crucible containing $\sim$5mg MoO$_3$ ($\geq$99.998% Alfa Aesar). This is loaded into a 32mm outer diameter quartz tube placed in a split-tube three-zone furnace. A second crucible containing 350mg sulfur ($\geq$ 99.99% purity, Sigma Aldrich) is located upstream from the growth substrates. Ultrahigh-purity Ar is used as carrier gas at atmospheric pressure. The procedure is: ramp the temperature to 300°C with 200sccm Ar flow, set to 300°C for 10mins, ramp to 700°C (50°C/min increase temperature rate) with 10sccm Ar flow, set at 700°C for 10 min, cool to 570°C with 10sccm of Ar, increase the gas flow to 200sccm and open the furnace for rapid cooling. SLG is grown on a 35µm Cu foil, following the process described in Ref. 51. The substrate is annealed in hydrogen atmosphere (H$_2$, 20sccm) up to 1000°C for 30 minutes. Then, 5sccm CH$_4$ is added to initiate growth. The sample is then cooled in vacuum (1mTorr) to room temperature and removed from the chamber.

Prior to assembling the SLG/MoS$_2$ stack, the quality and uniformity of MoS$_2$ on sapphire and SLG on Cu are inspected by Raman spectroscopy and photoluminescence (PL), using a Horiba Jobin Yvon HR800 spectrometer equipped with a 100X objective. The laser power is kept below 100µW (spot size < 1µm in diameter) to avoid possible heating effects or damage. Fig.3a (green curve) plots the Raman spectrum of CVD MoS$_2$ on sapphire for 514nm excitation. The peak at $\sim$385cm$^{-1}$ corresponds to the in-plane ($E_{2g}^1$) mode, while that at $\sim$404cm$^{-1}$, is the out of plane
(A1g) mode,63,64 with full width at half maximum FWHM(E1g)=2.5 and FWHM(A1g)=3.6 cm⁻¹, respectively. The E1g mode softens, whereas the A1g stiffens with increasing layer thickness,65,66 so that their frequency difference can be used to monitor the number of layers.65 The peak position difference~20 cm⁻¹ is an indicator of 1L-MoS2.65 The peak at~417 cm⁻¹ (marked by asterisk in Fig.3a) corresponds to the A1g mode of sapphire.67

Figure 3: (a) Raman spectra at 514 nm for 1L-MoS2 on sapphire, 1L-MoS2 on PET, and SLG/1L-MoS2. (b) Comparison at 514 nm of the Raman spectra of as-grown SLG on Cu (magenta curve) with SLG/1L-MoS2 after transfer on PET. (c) Raman spectra at 514 nm of PET substrate (black curve), 1L-MoS2 on PET (red curve) and SLG/1L-MoS2 on PET (blue curve).

The Raman spectrum measured at 514 nm of SLG on Cu is shown in Fig.3b (magenta curve). This is obtained after the removal of the non-flat background PL of Cu.68 The two most intense features are the G and the 2D peak, with no significant D peak. The G peak corresponds to the E2g phonon at the Brillouin zone centre.69 The D peak is due to the breathing modes of sp² rings and requires a defect for its activation by double resonance.69–72 The 2D peak is the second order of the D peak.69 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.69 In our sample, the 2D peak is a single sharp Lorentzian with FWHM(2D)~26 cm⁻¹, a signature of SLG.70 Different (~20) 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)~16 cm⁻¹. The
2D peak position, Pos(2D) is $\sim 2705\text{cm}^{-1}$, while the 2D to G peak area ratio, indicating a p-doping $\sim 300\text{meV}$, which corresponds to a carrier concentration $\sim 6 \times 10^{12}\text{cm}^{-2}$.

Another evidence for 1L-MoS$_2$ comes from the PL spectrum [Fig.4a (green curve)], showing a peak $\sim 658\text{nm}$ ($\sim 1.88\text{eV}$), due to band-to-band radiative recombination in 1L-MoS$_2$.\cite{75}

![Figure 4: (a) PL spectrum at 514nm (2.41eV) of 1L-MoS$_2$ on sapphire, and SLG/1L-MoS$_2$ after transfer on PET. (b) PL spectra of PET substrate (black curve), 1L-MoS$_2$ on PET (red curve) and SLG/1L-MoS$_2$ on PET (blue curve).](image)

Then, the MoS$_2$ film is transferred onto a PET substrate from sapphire using a KOH-based approach.\cite{61} The samples are first spin coated with $\sim 100\text{nm}$ polymethyl methacrylate (PMMA). This is detached in a 30% KOH solution, washed in DI water and transferred onto PET. The PMMA is then dissolved in acetone. Subsequently, SLG is transferred on the 1L-MoS$_2$ on PET. PMMA is spin coated on the SLG/Cu substrate, then placed in a solution of ammonium persulfate (APS) in DI water until Cu is etched.\cite{51,76} The PMMA membrane with attached SLG is then transferred to a beaker filled with DI water for cleaning APS residuals. The membrane is subsequently lifted with the target PET substrate having 1L-MoS$_2$ on top. After drying, PMMA is removed in acetone leaving SLG on 1L-MoS$_2$.

Raman and PL characterizations are performed at each step of the SLG/1L-MoS$_2$ assembly.
on PET, i.e on 1L-MoS$_2$ transferred on PET, and on SLG on 1L-MoS$_2$. This is to confirm no degradation during the fabrication process. For 1L-MoS$_2$ on PET, the Raman at 514nm is shown, with a close-up of the $E_{2g}^1$ and $A_{1g}$ regions, in Fig.3a (red curve). The frequency difference between $E_{2g}^1$ and $A_{1g}$ and the FWHMs are preserved on PET, suggesting no degradation. The PL spectrum of 1L-MoS$_2$ on PET is shown in Fig.4b (red curve). The signal from 1L-MoS$_2$ is convolved within the background due to the PET substrate [Fig.4b (black curve)]. In order to reveal the underlying PL signature of 1L-MoS$_2$, we use a point-to-point subtraction between the spectrum of 1L-MoS$_2$ on PET [Fig.4b (red curve)] and the reference PET spectrum [Fig.4b (black curve)]. Prior to subtraction, the spectra are normalized to the intensity of the Raman peak at $\sim 1615\text{cm}^{-1}$ (corresponding to the peak at $\sim 560\text{nm}$ in Fig.4b), due to the stretching vibrations of benzene rings in PET. As a result, the PL signal of 1L-MoS$_2$ can be seen in Fig.4a (blue curve) revealing no significant changes after transfer. The subsequent transfer of SLG on 1L-MoS$_2$ does not alter the 1L-MoS$_2$ PL position and lineshape [Fig.4b (blue curve)].

We then characterize the SLG transferred on 1L-MoS$_2$/PET. The intense Raman features of the underlying PET substrate [Fig.3c (black curve)], mask the SLG peaks. In order to reveal the Raman signatures of SLG, we first measure the reference spectrum, shown in Fig.3c (black curve), of a PET substrate, using identical experimental conditions as those for SLG/1L-MoS$_2$/PET. We then implement a point-to-point subtraction, normalized to the intensity of the PET peak at $\sim 1615\text{cm}^{-1}$, of the PET reference spectrum from the total spectrum Fig.3c (blue curve). The result is in Fig.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. Pos(G) is $\sim 1583\text{cm}^{-1}$, 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 $\sim 4 \cdot 10^{12} \text{cm}^{-2}$ ($\sim 250\text{meV}$).53,73

We then measure the absorption and transmission of SLG/1L-MoS$_2$ using a broadband (400-1300nm) 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. Fig.5a plots
Figure 5: (a) Transmittance of PET (black curve), 1L-MoS$_2$ on PET (red curve) and SLG/1L-MoS$_2$ on PET (blue curve). (b) Absorbance of 1L-MoS$_2$ and SLG/1L-MoS$_2$ as derived from the transmittance measurements. Dashed lines indicate our test wavelength.

The optical transmittance of bare PET ($T_{PET}$, black line), 1L-MoS$_2$ on PET ($T_{MoS_2}$, red line) and the final SLG/1L-MoS$_2$ stack on PET ($T_{Hetero}$, blue line) measured in the 400-800nm wavelength range. Fig.5b plots the absorption of 1L-MoS$_2$ on PET ($Abs_{MoS_2}$, red line) and of SLG/1L-MoS$_2$ on PET ($Abs_{Hetero}$, blue line), calculated as $Abs_{MoS_2}=(T_{PET}-T_{MoS_2})/T_{PET}$ and $Abs_{Hetero}=(T_{PET}-T_{Hetero})/T_{PET}$. The three peaks in Fig.5b at $\sim$650nm (1.91eV), $\sim$603nm (2.06eV), and $\sim$428nm (2.90eV) correspond to the A, B, C excitons of 1L-MoS$_2$.\textsuperscript{75,78} The positions of the A, B and C peaks remain unchanged after SLG transfer. The $Abs$ difference between the two curves (red and blue) is $\sim$2.6%, consistent with the additional SLG absorption.\textsuperscript{79}

The PD area is shaped by etching, whereby SLG extending beyond the 1L-MoS$_2$ layer is removed in an oxygen plasma. The source-drain and gate electrodes are then defined by patterning the contacts area, followed by Cr/Au (6nm/60nm) evaporation and lift-off. PDs with different channels lengths (100$\mu$m-1mm), 2mm channel width and common side-gate electrodes (1cm x 0.5cm) are built, Fig.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, high-k dielectrics (Al₂O₃, HfO₂), chemical dopants, ionic liquids and polymer electrolytes (PE). In order to gate our SLG/1L-MoS₂ on PET, we employ the latter due to its compatibility with flexible substrates and the ability to substantially dope SLG (±0.8eV) using small gate voltages (up to 4V), unlike other gating techniques, which would require considerably higher biases to reach the same doping. We use a PE consisting of LiClO₄ and polyethylene oxide (POE). We place the PE over both the SLG channel and the side-gate electrode. To evaluate the effect of PE deposition on the SLG channel doping we use Raman analysis (Pos(G)~1583cm⁻¹, FWHM(G)~19cm⁻¹, Pos(2D)~2686cm⁻¹ and A(2D)/A(G)~5.3, p-doping ~230meV) and find a small reduction of p-doping. For electrical measurements we apply −1V < VGS < 1V in order to avoid electrochemical reactions, such as hydrolysis of residual water in the electrolyte. These reactions may permanently modify the graphene electrode, and compromise the stability and performance of the device. To control the stability of the PE gating we continuously monitor the gate leakage current (Igate) and obtain Igate < 1nA throughout the experiments. The devices were tested~30 times, showing no degradation in the leakage current over at least six months.

We characterize the responsivity at 642nm (~1.93eV), slightly above the A exciton peak, where absorption of 1L-MoS₂ is maximized (Fig.5b). At 642nm the SLG/1L-MoS₂ heterostructure shows~8% absorption (Fig.5b) and the device retains~82% transparency (Fig.5a).

The IDS − VGS measurements in Fig.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 Po ranging from 100µW to 4mW. At these Po and with VDS = 0.1V we measure a positive VCNP ranging from ~0.39V to 0.47V, indicating an initial SLG p-doping~220meV, consistent with the Raman estimate.

Fig.6a shows that, for −1V < VGS < 0.5V where SLG transport is hole dominated, the current decreases under illumination (~10µA at VGS = −1V), as anticipated from the band-diagram of Fig.2. For VGS > 0.5V, where SLG is electron-doped, the PD shows a small (up to ~0.2µA) current increase under illumination. Fig.6b plots Rext as a function of VGS, as derived from transcon-
Figure 6: a) Transfer characteristics as a function of $P_o$. b) $R_{ext}$ as a function of $V_{GS}$ and $P_o$. Channel length and width are 100$\mu$m and 2mm respectively.

Electrical conductance measurements using:\(^{19}\)

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

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 Fig.2, $R_{ext}$ tends to increase for more negative $V_{GS}$, up to $\sim 5.5A/W$ at $V_{GS} = -1V$, $V_{DS} = 0.1V$ for $P_o = 100\mu W$. By taking into account that only 8% of light is absorbed ($P_{abs} = 0.08 \cdot P_o$), we derive $R_{int} = R_{ext} / 0.08 = 69A/W$. Fig.6b implies that the higher $P_o$, the lower $R_{ext}$. This can be explained considering that the more photo-generated 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 $R_{ext}$ to decrease.

Given that $R_{ext}, R_{int} > 1A/W$, we expect a photoconductive gain ($G_{PD}$),\(^{19,87}\) whereby absorp-
tion of one photon results in multiple charge carriers contributing to $I_{ph}$. Our PDs act as optically-gated photoconductors, where the SLG conductance is modulated by optical absorption in the 1L-MoS$_2$. In this configuration, the presence of $G_{PD}$ 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, $G_{PD}$ can be estimated as the ratio of electrons recombination ($\tau_{rec}$) and transit ($t_{tr}$) times in the SLG channel: $G_{PD} = \frac{\tau_{rec}}{t_{tr}}$. For higher $V_{DS}$, the free carriers drift velocity $v_d$ in the SLG channel increases linearly with bias (Ohmic region) until it saturates, because of carriers scattering with optical phonons. The linear increase in $v_d$ results in shorter $t_{tr}$, with $t_{tr} = L/v_d$, where $L$ is the channel length. Therefore, $G_{PD}$ is also expected to grow linearly with $V_{DS}$, providing higher $R_{ext}$. To confirm the photoconductive nature of $G_{PD}$ in our devices and test the dependence of $R_{ext}$ on $V_{DS}$, we measure $I_{DS} - V_{DS}$ under illumination at $P_o = 100\mu W$ for $V_{GS} = -1V$ and calculate $R_{ext}$ using Eq.1. The $I_{DS} - V_{DS}$ characteristics of the PD show linear dependence, confirming Ohmic behavior of the metal-SLG-metal channel. We use $V_{DS} < 1V$ to keep the device operation in the linear (Ohmic) regime and minimize the effects of the non-linear dependence of $v_d$ on $V_{DS}$ (such as velocity saturation) that might appear for $V_{DS} > 1V$. As shown in Fig.7, $R_{ext}$ scales with $V_{DS}$ and reaches $\sim 45.5A/W$ ($R_{int} \sim 570A/W$) at $V_{DS} = 1V$. This is almost one order of magnitude higher than at $V_{DS} = 0.1V$, consistent with the similar increase in $V_{DS}$. These results are at least two orders of magnitude higher than semiconductor flexible membranes. Furthermore, such combination of high (hundreds A/W) responsivity with $\mu A$ range photocurrent overcome 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 device has $R_{ext} \sim 2mA/W$, which is four 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 (642nm) as for opto-electronic characterizations. We scan areas of $80\mu m \times 140\mu m$ (pixel size $3\mu m \times 3\mu m$) at different locations. At each
Figure 7: $R_{\text{ext}}$ as a function of $V_{DS}$ for $P_o = 100 \mu W$ at $V_{GS} = -1V$.

position (pixel) the device photocurrent is measured (Fig.8a), while $V_{DS}=0.3V$ is applied. We also collect the backscattered light to give a reflection map (Fig.8b). Fig.8a indicates that the entire channel area confined between the source-drain electrodes is photoactive and shows uniform photocurrent photoresponse 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.

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).

We define $G_{PD}$ as the ratio between electrons recirculating in the SLG channel, thus sustaining
\( G_{PD} = \frac{|I_{light} - I_{dark}|}{q \cdot A_{PD} \cdot \Delta n_{ch}} \) (2)

where \( q \) is the electron charge and \( \Delta n_{ch} \) is the concentration per unit area of the injected electrons. \( \Delta n_{ch} \) is equal to the trapped-hole concentration in 1L-MoS\(_2\), which is related to a charge neutrality point shift \( \Delta V_{GS} = \Delta V_{CNP} \) in the transfer characteristics. To calculate \( \Delta n_{ch} \), we first write the potential balance in the metal-dielectric-SLG structure. When \( V_G \) is applied, it creates a gate-to-channel potential drop (\( V_{diel} \)), and it induces a local electrostatic potential in the graphene channel (\( V_{ch} = E_F / q \)):\(^{19,53}\)

\[
V_G = V_{diel} + V_{ch} = \frac{Q}{C_G} + V_{ch}
\] (3)

where \( Q \) and \( C_G \) are the charge concentration and the geometrical capacitance per unit area associated with the gate electrode respectively. \( |Q| = |q \cdot n_{ch}| \), reflecting the charge neutrality of the gate capacitor, with \( n_{ch} \) the charge carrier concentration per unit area in the channel. Any variations \( \Delta n_{ch} \) change \( \Delta V_G \). As a result:

\[
\frac{dV_G}{dQ} = \frac{1}{C_G} + \frac{dV_{ch}}{dQ}
\] (4)

which leads to:

\[
\Delta Q = (1/C_G + 1/C_Q)^{-1} \cdot \Delta V_G
\] (5)

where \( C_Q = dQ / dV_{ch} \) is the SLG quantum capacitance\(^{90,91}\) that characterizes the changes of the channel potential \( \Delta V_{ch} \) as a result of additional gating \( \Delta Q \), and \((1/C_G + 1/C_Q)^{-1} \) is the total capacitance \( C_{tot} \).

To calculate \( Q \) we first need to find \( C_G \) and \( C_Q \). In PE gating, \( C_G \) is associated with the EDL at the SLG/electrolyte interface.\(^{53,90,92,93}\) The EDL acts like a parallel-plate capacitor with a dielectric layer thickness of the order of \( \lambda_D \), so that \( C_G = C_{EDL} = \varepsilon \varepsilon_0 / \lambda_D \), 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\(^{94}\) if the electrolyte concentration is known. However, in the presence
of a polymer matrix, the electrolyte ions can form complexes with polymer chains,\textsuperscript{95} therefore the precise ion concentration is difficult to measure. For PE gating, different EDL thicknesses in the range $\sim 1 \sim 5\text{nm}$ have been reported.\textsuperscript{53,54,92,93} To estimate $C_{EDL}$ in our devices we take $\lambda_D \sim 2\text{nm}$\textsuperscript{53} and the dielectric constant of the PEO matrix to be $\varepsilon \sim 5$,\textsuperscript{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 $C_Q$.\textsuperscript{90} Therefore the latter cannot be neglected in Eq.5. $C_Q$ is given by:\textsuperscript{90}

$$C_Q \approx \frac{2q^2}{h v_F \sqrt{\pi}} \cdot \sqrt{n_{ch} + n_i}$$ \hspace{1cm} (6)

where $h$ is the reduced Planck constant, $v_F = 1.1 \cdot 10^6 m/s$ is the Fermi velocity of charge carriers in graphene,\textsuperscript{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.\textsuperscript{90,98–100} Using Raman and transconductance we estimate $n_i \sim 3 \cdot 10^{12} cm^{-2}$. From Eq.6 we then get $C_Q = 4 \cdot 10^{-6} F/cm^2$ at $V_{CNP}$. From Fig.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 $4 \sim 8 \cdot 10^{11} cm^{-2}$ 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 Fig.9. As discussed previously, $G_{PD}$ becomes larger for higher $V_{DS}$. Thus, we measure an increase of almost one order of magnitude ($G_{PD} \sim 4 \cdot 10^5$ at $P_o = 100\mu W$) for $V_{DS}$ going from 0.1V to 1V.

Finally, we test $I_{ph}$ as a function of bending using a Deben Microtest three-point bending setup (Fig.10a). The bending radius $r_b$ is estimated as $r_b = \left(\frac{h^2 + (L/2)^2}{2h}\right)$, 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 $r_b$ ($I_{ph,\text{bend}}$) are normalized to the value of $I_{ph}$ measured at rest with the sample in flat position ($I_{ph,\text{rest}}$). Fig.10b plots the normalized $I_{ph,\text{bend}}/I_{ph,\text{rest}}$ for different $r_b$, showing deviations within 15% for $r_b$ down to 1.4cm. Our value of $r_b$ is comparable to that reported for semiconductor membrane PDs,\textsuperscript{4,15} yet the latter show two orders of magnitude lower ($< 0.3 A/W$) responsivities.\textsuperscript{4,15} Although our $r_b$ is five times larger than the one reported by
flexible single NW devices,

3,16–18 the device area of the tested PD (> 40mm²) is at least six orders of magnitude larger compared to the single NW devices (< 5µm²). To test the device performance upon bending cycles, we first re-measure the photocurrent at rest (I_{ph,rest}, flat position) and then at the maximal bending (i.e smallest bending radius) allowed by our setup (I_{ph,bend} bending radius 1.4cm), repeating these measurements for 30 bending cycles. Fig.10c plots I_{ph,bend}/I_{ph,rest} as function of bending cycles. This shows that our PDs retain stable photocurrent after multiple bending tests with a I_{ph,bend}/I_{ph,rest} standard deviation ±12%.

Conclusions

We reported polymer electrolyte gated flexible photodetectors for visible wavelengths with external responsivity up to ~45.5A/W, photoconductive gain of 4 × 10^5, operation voltage < 1V and optical transparency > 82%. The responsivity is at least two orders of magnitude higher than in semiconductor flexible membranes. The devices show stable performance upon bending for radii of curvature larger than ~1.4cm. Owing to their responsivity, flexibility, transparency and low operation voltage, our photodetectors can be an attractive candidates to be integrated in wearable, biomedical and low-power opto-electronic applications.11,12,17
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 $I_{ph,rest}$ upon several bending cycles
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