

Ultrahigh Photogain Nanoscale Hybrid Photodetectors

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Detecting the intensity and the wavelength of natural light is of great importance to a host of applications at the frontier of science and engineering including fiber optic communication, surveillance, optical quantum information technology, and chemical or biological sensing.^[1,2] These applications place extreme demands on detector performance that highly depends on the active materials and the device architectures used. Previous reports^[3] show that the photodetector performance, such as the on/off ratio,^[4-6] responsivity,^[7,8] detectivity,^[9,10] and quantum efficiency,^[11,12] can be improved when the device dimensions are scaled down to the nanoscale. Despite these efforts, however, how the device architectures affect the photodetector performance still remains ill-understood, hampering the development of high-performance photodetectors. Here, we demonstrated a class of ultrahigh photogain nanoscale hybrid photodetectors formed from carbon electrode-molecule junctions (CEMJs) using the blend of poly(3-hexylthiophene) and [6,6]-phenyl-C₆₁-butvric acid methyl ester (P3HT:PCBM) as photoresponsive semiconductors. The unique device architecture, tunability of nanoscale channel lengths, and the optimized contact nature of semiconductor/electrode interfaces led to the device operation at room temperature and at very small operating voltages (≤ 10 V). This produced ultrahigh photogains of over 10^3 when graphene was used as electrodes and over 10^6 when single-walled carbon nanotubes (SWNTs) were used as electrodes. Such a CEMJ-based photodetector may become a

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fundamental device platform for optical information and sensing applications, thus offering new insights for innovations that can be applied to many other technologies such as multifunctional organic electronics, digital communication between optical and electrical signals, and logic circuits.

The ability to determine the number of photons is a key parameter to quantify the performance of photodetectors.^[13] This number of photons can be determined by using the principle that the photoinduced current is proportional to the number of photons absorbed. The larger the proportion, the better the resolution will be. The external quantum efficiency (EQE or photogain),^[11,12] which determines how many carriers are generated by a single absorbed photon.^[14] can be used to calculate this proportion. Therefore, the external quantum efficiency is an important figure of merit for evaluating the photodetectors. Today, discrete sensors or materials that were used to build different photodetectors exhibit high detectivity of greater than 10¹² cm Hz^{1/2}/W and some are able to extend the range of optical detection from the UV to the infrared. In general, inorganic thin-film-based photodetectors require expensive fabrication techniques and have a high detectivity when they are cooled down to a low temperature (4.2 K);^[13] InAs nanowire-based photodetectors showed high photogains from ultraviolet to nearinfrared at room temperature, but need complex molecular beam epitaxy (MBE) techniques;[15-17] Colloidal inorganic semiconductor quantum-dot-based photodetectors need high operating voltages (>40 V) because of the use of an "inplane" device structure with electrode spacing of >5 µm.^[10] Other polymer photodetectors lack a high quantum efficiency (they are limited to an efficiency of <70%) although they exhibit broad spectral response from 300 to 1450 nm with a high detectivity.^[2] Therefore, low-cost photodetectors with a high quantum efficiency that are capable of operating at room temperature with a small driving voltage are rare. These limitations substantially hamper their applications in both industrial and scientific communities.

To overcome these limitations, we first fabricated P3HT:PCBM hybrid photodetectors based on CEMJs with high-quality chemical vapor deposition (CVD)-grown single-layer graphene (SLG) as the nanoelectrodes. We chose P3HT:PCBM hybrids as photoactive candidates because the blend of conductive polymers and fullerene derivatives has become a model system widely used in organic heterojunction solar cells and photodetectors since the initial discovery of photoinduced electron transfer from a conducting polymer to a fullerene.^[18] **Figure 1**a shows the typical device structure, where SLG is precisely cut using electron beam lithography

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Figure 1. Device structure of CEMJ-based hybrid photodetectors and energy-level diagram of P3HT:PCBM blends. a) The device structure. P3HT:PCBM blends were spin-coated over the graphene electrodes that had a small-gap length. These electrodes were lithographically formed with tunable gap lengths. b) The molecular structures of P3HT and PCBM (top) and the UV–vis spectra (bottom) of thin films of pristine P3HT, pristine PCBM, and the P3HT:PCBM blend (weight ratio 1:1) on quartz substrates. c) The energy-level diagram of P3HT, PCBM, and graphene. Under illumination, the photogenerated excitons diffuse to the P3HT/PCBM interface to efficiently dissociate into free electrons and holes. These free carriers can be transported in the active layer in opposite directions and are finally collected by the graphene electrodes.

on silicon wafer substrates, thus forming 2D graphene electrodes with tunable gap lengths (*l*). The P3HT:PCBM blend was then spin-coated to bridge the electrodes. The fabrication processes are presented in the Figure S1–S2 (Supporting Information).^[19,20] The UV–vis absorption spectra of pristine P3HT, PCBM, and P3HT:PCBM composites as well as their molecular structures are shown in Figure 1b. P3HT thin films have a broad absorption in the visible region, mainly from 400 to 650 nm, while PCBM thin films mainly absorb in the UV region with an absorption peak at ~330 nm. When P3HT is mixed with PCBM with a weight ratio of 1:1, the P3HT:PCBM composites exhibit a broad absorption in the UV–vis region. This broad absorption is a simple addition of the P3HT and PCBM absorption, which favors efficient photon absorption and exciton generation.^[21,22]

Another important design we should emphasize is the use of graphene as electrodes instead of metals. This is because graphene is entirely composed of carbon atoms and has a low work function of 4.7–4.9 eV.^[23] This work function range would be a good match to the energy levels of the organic semiconductors, leading to the formation of a good contact interface between graphene and the P3HT:PCBM blends. This reduces the Schottky barrier for charge injection. As demonstrated in the energy-level diagram in Figure 1c, due to the large differences between the highest occupied molecular orbital/lowest unoccupied molecular orbital (HOMO/ LUMO) energy levels of P3HT and PCBM, an electric field is formed at the P3HT/PCBM interface. Photons that are absorbed inside the device excite P3HT, leading to the creation of excitons. These excitons diffuse to the P3HT/PCBM

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interface and then are dissociated into free electrons and holes driven by the electric field at the interface. These free carriers can be transported in the active layer and finally collected by the graphene-based electrodes efficiently.^[6,18,21] In conjunction with the remarkable electronic properties of graphene,^[24] the improved molecule/graphene interfaces place SLG as an ideal electrode for building new types of molecular electronic devices.^[25–27] The matched energy-level alignments at either the molecule/electrode interface or the P3HT/PCBM interface are a harbinger for the high device performance described below.

Figure 2a shows the source-drain current $(I_{\rm D})$ as a function of wavelength for hybrid photodetectors with a 200-nm gap length. The gap length is shown in the inset of Figure 2a. The devices exhibit a broad spectral detection range from the UV to the visible that matches the UV-vis absorption spectrum of the P3HT:PCBM blend (blend ratio 1:1 by weight) and reliable cycling responsive stability. More reproducible data for devices with different gap lengths can be found in the Figure S3-S5 (Supporting Information). The average response and recovery times of the photodetectors are \approx 400 ms and \approx 20 s, respectively. Control experiments using graphene electrodes either in the absence of the P3HT:PCBM blends or only with PCBM or P3HT only have little photoresponse (Figure S6-S8). Also, we found that the P3HT:PCBM blends absorbed on the pristine graphene surface do not contribute to the device photoresponses (Figure S9-S10, Supporting Information). These results consistently demonstrate that the P3HT:PCBM blends sandwiched between graphene electrodes dominate the device photoresponse. The calculated responsivity and detectivity are high at about 10^3 A W⁻¹ and 10^8 cm Hz^{1/2}/W, respectively. The strong photoresponse mostly originates from the miniaturized device architecture and the good contact nature of semiconductor/electrode interfaces as demonstrated previously.^[7] In this study, we will focus on the exploration of another figure of merit for photodetectors, the EQE (η) , which is defined according to the Garrido's gain model^[28] by

$$\eta(\text{photogain}) = \left(\frac{I_{\text{ph}}/q}{P_{\text{in}}/h\nu}\right) \times 100\% = \frac{I_{\text{ph}}}{P_{\text{in}}\lambda} \times 124\%$$
(1)

where I_{ph} (measured in A) is the photocurrent generated by a light beam with an input power P_{in} (measured in watts) falling onto the active area of the photodetector.^[14] The constant q is the electronic charge, and h is the Planck's constant. The frequency, v, of the incident photon can be used to calculate its wavelength, λ . According to this formula, the EQE of the P3HT:PCBM hybrid photodetectors with the graphene gap length of 200 nm was about 922 (or 92200%) at the maximum absorption wavelength of 540 nm with a light intensity, I_{light} , of 12.8 W m⁻²) and a source-drain bias voltage of -10 V (Figure S3 and S11, Supporting Information). This value is higher than those using gold as electrodes under the same conditions (Figure S12, Supporting Information), proving that SLG is better suited as electrode materials for organic optoelectronic devices. Unfortunately, the on/off ratio of these devices was relatively low (approximately 2),





Figure 2. Photoresponsive properties of graphene-based P3HT:PCBM hybrid photodetectors. a) Comparison of the wavelength–dependent spectrum of photocurrents with the UV–visible absorption spectrum of P3HT:PCBM blends at a gate voltage (V_G) of 0 V and a source-drain voltage (V_D) of -1 V. Light was scanned from 300 to 750 nm in 1-nm steps with each wavelength held for 1 s. The inset shows the gap size (\approx 200 nm) of the graphene electrodes. Unless otherwise specified, the channel width is 36 µm. We found that the EQE has a negligible dependence on the channel width (Figure S15, Supporting Information). b) The linear fits of EQEs and the source-drain bias voltage at gap lengths of 50, 100, 200, and 400 nm (λ = 540 nm; V_G = 0 V). c) The linear fits between EQEs and the reciprocal of the square of the gap length at different values of V_D (-0.1 V, -0.5 V, and -1 V) (λ = 540 nm; V_G = 0 V).

most likely due to the short-channel effect and thus weak gating capability.^[7,8]

Assuming that the transport of free carriers in the P3HT:PCBM layer is mainly controlled by a "hopping" mechanism,^[29] the transport of the free carriers in the active layer is strongly dependent on both the driving voltages



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 $(V_{\rm D})$ and the hopping distance, that is, the distance between the source and the drain (l). To optimize the η values, it is important to determine the relationship between η , $V_{\rm D}$, and *l*. We found that the EQE increased when the gap length decreased or the source-drain bias voltage became large (Figure S13, Supporting Information). Linear fitting was used to study the quantitative relationship between η and $V_{\rm D}$. Figure 2b shows that the EQE value is proportional to the source-drain bias voltage, and the highest η achieved from these graphene-based hybrid photodetectors reached about 10^3 (or 100000%). This is reasonable because the driving force determines the velocity of the charge carriers under certain working conditions (for example, constant power under illumination and the gap length). The higher the operating voltage, the faster the carrier moves in the conducting channel.

After clarifying the relationship between η and $V_{\rm D}$, we explored the quantitative relationship between η and l. We summarized the correlation coefficients (R^2) of the linear fit of the EQE to the reciprocal gap length (1/l) when the exponent of 1/l varies from 1 to 5 (Figure S14, Supporting Information). The correlation coefficient was the highest when exponent was 2, suggesting that the EQE is inversely proportional to the square of the gap length l. That is, there is a linear relationship between the EQE and the reciprocal of the square of the gap length as shown in Figure 2c. In summary, the EQE is proportional to the source-drain bias voltage and inversely proportional to the square of the gap length, respectively. This relation can be expressed by the following equation

$$\eta \propto \frac{V}{l^2} \tag{2}$$

where V is the source-drain bias voltage and l is the gap length. To date, there is no report quantitatively showing the intrinsic relationship between η and V_D/l and this equation provides clear insights for designing new types of photodetectors and improving the photoresponse.

To further define the relationship between the EQE, the source-drain bias voltage and the gap length, we introduce another gain factor (G),^[14] defined by

$$G = \frac{\tau_{\rm c}}{\tau_{\rm t}} \tag{3}$$

where τ_c is the lifetime of the photogenerated carriers, and τ_t is the time required for the carriers moving from one electrode to another. Because this distance is the gap length *l*, the transit time, τ_t , can be expressed as

$$\tau_{\rm t} = \frac{l}{v_{\rm d}} \tag{4}$$

where v_d is the drift velocity of carriers. Also, the carrier mobility, μ , which characterizes the drift velocity, v_d , of carriers when driven by an electric field, *E*, is given by

$$\mu = \frac{v_{\rm d}}{E} = \frac{v_{\rm d}}{\frac{V}{l}} = \frac{v_{\rm d} \cdot l}{V} \tag{5}$$

By substituting Equation (4) into Equation (5), we obtain

$$\mu = \frac{\frac{l}{\tau_{t}} \cdot l}{V} = \frac{l^{2}}{\tau_{t} \cdot V} \tag{6}$$

Then, by substituting Equation (6) into Equation (3), the factor G, can be rewritten as

$$G = \frac{\tau_c \mu V}{l^2} \tag{7}$$

Considering the fact that τ_c and μ are the intrinsic properties of the materials, this formula can be used in conjunction with Equation (2) to explain our experimental data.

On the basis of this relationship, it can be deduced that for photoactive materials with a longer τ_c and a greater μ , η can be high. For example, η can be approximately 10³ or higher if we further reduce the gap length and/or increase the source-drain bias voltage. To determine if this was correct, we tried to lithographically cut SLG with a gap length as short as possible. However, we found that the incision was irregular, which means that SLG was not suitable for use as electrodes for photodetectors. This is because the graphene ribbon has a width about 36 µm in our experiment, which leads to the extreme difficulty in uniformly cutting graphene with a gap length less than 50 nm. If the graphene ribbon width was decreased down to the nanoscale, a gap length of a few nanometers could be easily obtained. However, this graphene nanoribbon will then have semiconducting properties,^[30] and so it will be unsuitable for use as electrodes. We therefore chose another carbon allotrope, SWNTs, as candidates for electrodes. This is because SWNTs have the capability to form a good contact interface between SWNTs and the P3HT:PCBM blends because of the energy-level alignment at the interfaces. The SWNTs will have either metallic or semiconducting properties with natural diameters between 1 and 3 nm.^[31] Thus, we fabricated P3HT:PCBM hybrid photodetectors using metallic SWNTs as point contacts (Figure S17-S22, Supporting Information). The fabrication processes are presented in the Supporting Information.^[20] Figure 3a and Figure S23 (Supporting Information) present the device structure of SWNT-based hybrid photodetectors and the energy-level diagram at the interfaces. These devices have excellent cycling responsive stability (Figure S24, Supporting Information), good intensity-dependent photocurrent performance (Figure S25, Supporting Information) and a broad spectral detection range covering from the UV to the visible (Figure 3b and S26, Supporting Information). According to Equation (1), the optimum EQE of P3HT:PCBM hybrid photodetectors based on SWNT nanoelectrodes with a gap length of about 10 nm was calculated to be $\approx 3.55 \times 10^6$ (or 355000000%) at the maximum absorption wavelength of 540 nm with a light intensity, I_{light} , of 12.8 W m⁻² and a source-drain bias voltage 10 V. This high η

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Figure 3. Device structure and photoresponses of SWNT-based hybrid photodetectors. a) The device structure. b) Photocurrents as a function of wavelength and the UV-visible absorption spectrum of the P3HT:PCBM blend with a weight ratio of 1:1 ($V_G = 0$ V; $V_D = -10$ V). The light was scanned from a wavelength of 300 to 750 nm in 1 nm steps with each wavelength held for 1 s. The inset shows the gap size (\approx 10 nm) of SWNT electrodes with a \approx 2 nm diameter.

value might be due to an integrated mechanism, for example, owing to buildup of trapped charges at the semiconductor/ dielectric interface during illumination over tens of seconds and/or the explosion of photoinitiated migration of carriers stored in the active channel.

To show the importance of both l and V_D to the photoresponse, we investigated how different P3HT:PCBM blend ratios affect the EQE value with the same device structure. **Figure 4** shows the linear fit of the EQE and the sourcedrain bias voltage with different P3HT:PCBM blend ratios (1:2, 1:1, and 2:1) (Figure S26, Supporting Information). There was little difference in the photoresponses when the blend ratio changed, showing that the channel length and the source-drain bias voltage are the key parameters to optimize the EQE. The best responsivity and detectivity are high at about 10⁶ A W⁻¹ and 10¹³ cm Hz^{1/2}/W, respectively. The highest EQE value achieved from our systematic experiments so far was 6.49×10^6 (or 649000000%) at the maximum absorption wavelength of 540 nm and a source-drain bias voltage of -15 V.



Figure 4. Correlations between EQEs and P3HT:PCBM blend ratios. The EQE values were extracted from the data at the maximum absorption wavelength (\approx 540 nm; $I_{light} = 12.8$ W m⁻²) and the source-drain bias voltages (from -5 and -10 V to -15 V). The $V_{\rm G}$ was kept constant at 0 V.



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In conclusion, we have demonstrated a mature device platform for making high-performance hybrid photodetectors with ultrahigh EOEs (photogain) up to six orders of magnitude using sp^2 carbon nanomaterials as nanoscale electrodes. Even though several examples of P3HT:PCBM blend-based photodetectors have been published, none of the reported composite photodetectors have achieved ultrahigh photogain as reported in this work. We accomplished this task by systematically exploring the effect of the device architectures on the photodetector performance. Just like organic moleculebased photodetectors, despite numerous papers published in the field for many years, major advance is still possible for

better performance if new device architectures can be introduced. The achievement of such a high quantum efficiency implies that CEMJ-based photodetectors have the ability to resolve the number of photons,^[13] potentially providing a new generation of single-photon detectors operating at room temperature and at a low driving voltage. The ease of device fabrication in combination with the compatibility with conventional complementary metal oxide semiconductor (CMOS) technologies opens exciting opportunities for the creation of low-cost, high-density, high-performance detector arrays for a wide variety of future applications such as biomedical imaging, telecommunications, information security, optical quantum computation, and logic circuits.

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