Haiyan Nan, Fengqiu Wang, Xiaomu Wang, Yi Shi, and Xinran Wang*

National Laboratory of Solid State Microstructures, School of Electronic Science and Engineering, and Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093, China

School of Microelectronics, Xidian University, Xian 710071, China

Beijing Key Laboratory of Novel Thin Film Solar Cells, Renewable Energy School, North China Electric Power University, Beijing 1002206, China

Department of Physics, Southeast University, Nanjing 211189, China

Supporting Information

ABSTRACT: Interfacing light-sensitive semiconductors with graphene can afford high-gain phototransistors by the multiplication effect of carriers in the semiconductor layer. So far, most devices consist of one semiconductor light-absorbing layer, where the lack of internal built-in field can strongly reduce the quantum efficiency and bandwidth. Here, we demonstrate a much improved graphene phototransistor performances using an epitaxial organic heterostructure composed of perylene-3,4,9,10-tetracarboxylic dihydride (PTCDA) and pentacene as the light-absorbing layer. Compared with single light-absorbing material, the responsivity and response time can be simultaneously improved by 1 and 2 orders of magnitude over a broad band of 400−700 nm, under otherwise the same experimental conditions. As a result, the external quantum efficiency increases by over 800 times. Furthermore, the response time of the heterostructured phototransistor is highly gate-tunable down to sub-30 μs, which is among the fastest in the sensitized graphene phototransistors interfacing with electrically passive light-absorbing semiconductors. We show that the improvement is dominated by the efficient electron–hole pair dissociation due to interfacial built-in field rather than bulk absorption. The structure demonstrated here can be extended to many other organic and inorganic semiconductors, which opens new possibilities for high-performance graphene-based optoelectronics.

KEYWORDS: Organic semiconductors, graphene, heterostructure, phototransistors, two-dimensional

Graphene is a promising material for high-speed optoelectronics due to its broadband, tunable optical absorption and high carrier mobility. However, graphene itself has low light absorption (~2.3%) in the visible and near-infrared spectrum range. To build high-responsivity photodetectors, an effective strategy is to interface graphene with light-sensitive semiconductors. In these devices, the photoinduced electron–hole pairs are generated in the semiconductor, dissociated at the interface, and collected by graphene to give photocurrent. Various types of semiconductors have been used so far, such as quantum dots, nanocrystals, transition-metal dichalcogenides, organic small molecules/polymers, and perovskites. However, this type of devices naturally suffers from the photosensitivity (R)−response time (τ) trade-off. The deep traps in the light-absorbing layer cause ultrahigh photoconductive gain (G) and R but at the same time sacrifice the operational bandwidth. In addition, most graphene-based hybrid phototransistors consist of only one semiconductor light-absorbing layer. The lack of internal electric field (within the light-absorbing layer) can prevent the efficient separation of electron–hole pairs and cause low quantum efficiency (QE). As a result, the devices have to rely on long intrinsic τ (typically in the range of milliseconds to seconds without gate pulses) to achieve high R. Recently, several strategies using external field modulation have been put forward to remedy this trade-off. For example, the use of ferroelectric substrate or top transparent electrode can introduce a vertical field to increase the charge separation efficiency, while the ionic polymer gate can screen the charge traps and reduce the time response. However, these approaches involve more complex device fabrication processes, and the best devices can only operate at sub-1 ms time scale.

Here, we report the simultaneous optimization of R, τ, and QE of graphene-based phototransistors by rational design of heterostructure as the light-absorbing layer. Instead of using the external gate field to facilitate charge separation, here we exploit the intrinsic built-in electric field at the semiconductor interfaces. Taking organic oligomers PTCDA and pentacene as an example, we show that the graphene/PTCDA/pentacene (GPP) phototransistors can achieve R = 10^5 A/W, intrinsic τ = 1 ms. This is among the fastest in the sensitized graphene phototransistors interfacing with passive light-absorbing semiconductors. We show that the improvement is dominated by the efficient electron–hole pair dissociation due to interfacial built-in field rather than bulk absorption. The structure demonstrated here can be extended to many other organic and inorganic semiconductors, which opens new possibilities for high-performance graphene-based optoelectronics.

Received: July 31, 2017
Revised: August 26, 2017
Published: September 6, 2017

DOI: 10.1021/acs.nanolett.7b03263
Nano Lett. 2017, 17, 6391−6396
down to 28 μs, and internal QE (IQE) up to 64%. Compared to graphene/PTCDA, $R$, $\tau$, and QE all have huge improvement that are much beyond the combined absorption of each individual material. We find that the high-quality PTCDA/pentacene interface facilitates the formation of charge transfer (CT) states, which more effectively dissociates the electron–hole pairs generated in both materials and leads to much higher QE.

Following our previous works,9 the GPP phototransistors were fabricated by van der Waals (vdW) epitaxy on graphene field-effect transistors (FETs) in a vacuum tube furnace (see Experimental Section for details of fabrication). To avoid any organic residue and preserve the clean surface of graphene, the Au electrodes were mechanically transferred onto graphene without lithography.16 PTCDA has to grow first because it has higher evaporation temperature, therefore is stable during the subsequent pentacene growth. We performed atomic force microscopy (AFM) to obtain the topological information on each layer. Figure 1a and b shows the device schematics and AFM image of a typical GPP phototransistor (the pentacene does not cover the entire device for better clarity). Both PTCDA and pentacene are grown in a layer-by-layer fashion with ~0.3 nm and ~1.5 nm layer thickness, respectively (Figure 1f). The small height of the PTCDA layer suggests that it adopts the face-on packing as predicted theoretically and observed on epitaxial graphene.17–19 The height of pentacene, on the other hand, is consistent with the thin-film phase, suggesting that is has the usual herringbone-type packing.20 The PTCDA film often grows uniformly across the whole sample, while pentacene tends to nucleate near one electrode and extends to the other (Figure S1). The average thickness of PTCDA and pentacene ranges 4–20 nm and 1–3 nm in our GPP devices, respectively. Despite their distinct growth behavior, both materials are smooth and single-crystalline according to the cross-polarized optical micrographs (Figure S2), giving very high interface quality at both graphene/PTCDA and PTCDA/pentacene.

The combination of PTCDA and pentacene is chosen as the light-absorbing layer because of their complementary absorption spectrum in the visible range (Figure S3) as well as the
proving that the photoresponse is dominated by the oligomers. The summation of the absorption from PTCDA and pentacene, shown in Figure 1c. This con

dipoles and built-in electric field in the vertical direction as illustrated in Figure 2a. The wavelength-dependent surface potential is lowest and highest for pentacene and graphene, respectively, and only changes abruptly at the steps in the heterojunction. The band diagram is further corroborated by SKPM. Figure 1d shows the PL image of PTCDA (left) and PTCDA/pentacene heterostructure (middle), grown on boron nitride substrate, under otherwise the same experimental conditions. We observed uniform and bright PL from the PTCDA layer, but the luminescence was quenched on the heterostructure (except the uncovered PTCDA area, Figure 1d, right panel), indicating strong charge transfer as expected for the type-II heterojunction. The band diagram is further corroborated by SKPM. Figure 1e shows the corresponding AFM and SKPM images of a graphene/11-layer PTCDA/few-layer pentacene sample. The surface potential is lowest and highest for pentacene and graphene, respectively, and only changes abruptly at the steps (Figure 1f). This confirms that the formation of interface dipoles and built-in electric field in the vertical direction as shown in Figure 1c.

Next, we performed photocurrent measurements on GPP phototransistors (see Methods for details of measurements). Compared with phototransistors with single light-absorbing material (PTCDA or pentacene), a typical GPP device shows ~10-fold improvement in R over a broad band of 400–700 nm (Figure 2a). The wavelength-dependent R can be nicely fit by summation of the absorption from PTCDA and pentacene, proving that the photoresponse is dominated by the oligomers. The R of GPP devices can reach 10^7 A/W under low light intensity, while the graphene/PTCDA control device has a maximum R ~ 6.3 × 10^5 A/W, measurable only under much intense laser power (Figure 2b). The decrease of R at high incident power is consistent with other graphene phototransistors, which is due to the reduction of built-in field with a large number of photogenerated carriers. The poor performance of the control devices is consistent with the weak charge transfer between graphene and PTCDA, due to the relatively small energy misalignment. We note that all of the tests above were performed under negative 5 VGate (p-doping). Under positive 5 VGate on the other hand, the GPP devices showed a smaller R and much faster τ, while the photoresponse of graphene/PTCDA control devices was almost undetectable (Figure S5). The R-wavelength for a GPP device in both electron and hole branches, including at 500 nm (mainly by PTCDA) and 670 nm (mainly by pentacene) did not show strong dependence on the thickness of either material (Figure S8). Both evidence, together with the fact that the increase of R did not increase with the thickness of pentacene as long as a significant portion of the device area was covered by the heterostructure. In addition, the ratio of R at 500 nm (mainly by PTCDA) and 670 nm (mainly by pentacene) did not show strong dependence on the thickness of either material (Figure S8).

To understand whether the enhancement of R originates from bulk absorption effects or interfacial effects, we performed thickness-dependent studies on the same GPP phototransistor subject to repeated pentacene growth (Figure S7). We found that R did not increase with the thickness of pentacene as long as a significant portion of the device area was covered by the heterostructure. In addition, the ratio of R at 500 nm (mainly by PTCDA) and 670 nm (mainly by pentacene) did not show strong dependence on the thickness of either material (Figure S8). Both evidence, together with the fact that the increase of R occurred in a broad band beyond the absorption of either material (Figure 2a), points to interfacial effects as the main reason behind the improved performance, similar to organic donor–acceptor systems. We note that the shape of the R-wavelength varies from device to device (Figure 2a, Figures S7 and S9), which may depend on the detailed morphology and coverage of pentacene and PTCDA layers (Figure S9).
The dynamic response is another important aspect of phototransistors. The typical $\tau$ of PTCDA/graphene and pentacene/graphene phototransistors is hundreds and tens of milliseconds, respectively (Figure S10). Figure 3a shows the $\tau-V_g$ relationship of a representative GPP device (the same device as Figure 2a) under different laser wavelengths, obtained by exponential fitting of the photocurrent trailing edge (Figure 3b). Two different regimes are separated by $V_g = V_0$, which corresponds to the cross point between the transfer curves under dark and illumination (Figure S4a). In the hole branch ($V_g < V_0$), $\tau$ is on the order of several hundred $\mu$s, which is 2–3 orders of magnitude lower than the control devices. In the electron branch ($V_g > V_0$), $\tau$ is reduced by another order of magnitude to several tens of microseconds. Inside each regime, $\tau$ shows a weak $V_g$ and wavelength dependence. According to the absorption spectra (Figure S3), PTCDA and pentacene absorbs mostly in 400–500 nm and 600–700 nm, respectively, while they both have absorption in 500–600 nm. The wavelength independence suggests that the response time does not depend on which material the electron–hole pairs are generated, as expected from Figure 1c. The $\tau-V_g$ can be explained by the energy diagrams in Figure 3c. When $V_g > V_0$, graphene has a high density of electrons, which can easily diffuse back into the hole-rich pentacene, resulting in a short lifetime. When $V_g < V_0$, on the other hand, graphene is also electron-deficient, so it takes a much longer time for electrons to neutralize holes on pentacene.

In the electron branch, the intrinsic response time in our GPP devices can be as low as 28 $\mu$s (Figure 3a), which is, to the best of our knowledge, the fastest graphene phototransistors.

Figure 3. Dynamic response of GPP phototransistors. (a) $\tau-V_g$ relationship of the GPP device in Figure 2a. Blue squares, green triangles, and red circles represent 495, 550, and 670 nm laser illumination, respectively. (b) The dynamic response curves under 550 nm, $V_g = V_0 = -8$ V (top panel) and $V_g = V_0 = 10$ V (bottom panel). The solid lines are exponential fitting of the trailing edges. (c) The energy diagram of the recombination process for $V_g - V_0 > 0$ (left) and $V_g - V_0 < 0$ (right).

Figure 4. QE analysis. (a) The $I_{ph}-V_g$ characteristics of a GPP phototransistor under 550 nm laser illumination (blue squares) together with a theoretical fit using experimentally derived parameters (red dashed line). From the fitting, $EQE \sim 5.5\%$ is derived. (b) Statistical analysis of EQE of graphene/PTCDA devices at 550 nm and GPP devices at 670, 500, and 550 nm. The inset image is the IQE of GPP devices at 500 nm with different PTCDA thicknesses. For all devices, the laser power was as low as possible while maintaining good single-to-noise ratio. (c) Summary of device performance of sensitized graphene phototransistors with different semiconductors. Devices sensitized with single electrical passive light-absorbing layer are marked by the pink shadow. The red dashed line encircles the devices using vertical field. The blue region denotes GPP devices. The bandwidth is calculated by $BW = 1/2\pi\tau$. The absorption spectra (Figure S3), PTCDA and pentacene absorbs mostly in 400–500 nm and 600–700 nm, respectively, while they both have absorption in 500–600 nm. The wavelength independence suggests that the response time does not depend on which material the electron–hole pairs are generated, as expected from Figure 1c. The $\tau-V_g$ can be explained by the energy diagrams in Figure 3c. When $V_g > V_0$, graphene has a high density of electrons, which can easily diffuse back into the hole-rich pentacene, resulting in a short lifetime. When $V_g < V_0$, on the other hand, graphene is also electron-deficient, so it takes a much longer time for electrons to neutralize holes on pentacene.

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with electrically passive light-absorbing layers. The τ is almost 4 orders of magnitude smaller than solution processed organic/graphene phototransistors and 3 orders of magnitude smaller than our previously reported graphene/C8-BTBT devices. Considering the similar Iph rising and falling times (Figure 3b, S11), we expect that the GPP heterostructure can operate at over 5 kHz bandwidth. The extraordinary response time in the GPP phototransistors is most likely due to three aspects. From AFM and cross-polarized microscopy (Figure S1 and S2), the PTCDA and pentacene are highly crystalline, and their interface is atomically smooth. This leads to a low density of charge traps in the GPP phototransistors. Furthermore, the local molecular arrangements may facilitate charge transfer at the two interfaces. We speculate this may be the main reason that GPP is much faster than the graphene/C8-BTBT devices. Finally, the large smooth. This leads to a low density of charge traps in the GPP phototransistors. The key to further improve bandwidth is to design proper interface and remove charge traps in the device as much as possible.

In conclusion, we demonstrate the use of heterostructure as the light-absorbing layer to greatly enhance the performance of graphene-based phototransistors. Compared with individual light-absorbing semiconductors, the GPP heterostructure significantly improves R, τ, and QE at the same time. The performance improvement is due to the built-in field in the heterostructure which effectively separates the generated electron–hole pairs. We would like to point out that the PTCDA/pentacene combination is just one example of this concept. There are many other combinations of organic and inorganic semiconductors that fulfill similar band alignment. Furthermore, we expect that energy diagram with reverse built-in field would also work the same way by choosing appropriate materials (Figure S12).

Methods. GPP Device Fabrication and Characterization. We first fabricated backgated graphene field-effect transistors on 300 nm SiO2/Si substrates with Au electrode. The transistors were placed in a tube furnace to grow PTCDA and pentacene sequentially. Specifically, PTCDA (purchased from Sigma-Aldrich with a purity of 97% without further purification) and pentacene (purchased from TCI with a purity of 99% without further purification) powder were placed at the center of the furnace, and the graphene FETs were located downstream. The growth temperatures for PTCDA and pentacene were 230 and 120 °C, respectively, under 1 × 10−4 Torr vacuum. AFM and SKPM characterizations were performed by an Asylum Research Cypher system in ambient atmosphere. Conductive tips (Multi75E-G) coated with Cr/Pt biased at +3 V were used for SKPM. Under such condition, the material with a lower surface potential exhibits relatively smaller potential difference with the biased tip and shows up as a brighter color. Photoluminescence mapping was performed at 450 nm LED illumination, and PL signal is collected by a CCD equipped with a 500 nm high-pass filter.

Photo current Measurements. The spectral response measurement was done with a supercontinuum white-light laser source (Fianium WhiteLase SC400) in a close-cycle cryogenic vacuum probe station. The laser was collimated to a uniform 3 mm spot through an aperture. Photocurrents were detected by Keithley 4200 SMU modules, and Agilent 4156C was used to control the laser. The output Vg was measured from the photodetector. Time-resolved measurements were done with Thorlabs GVS212 and modulated photocurrent signals were amplified and detected using lock-in (Stanford SR830) technique. Photocurrent mapping was performed under 637 nm laser illumination which was modulated by a square-wave signal generator source.
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2013CBA01604 and 2015CB351900; 61575153; National Key Basic
Research Program of China
The authors declare no competing financial interest.
Notes
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ACKNOWLEDGMENTS
This work was supported in part by National Natural Science Foundation of China 61325020, 61521001, 61106079, 61575153; National Key Basic Research Program of China 2013CBA01604 and 2015CB351900; “Jiangsu Shuangchuan” program and “Jiangsu Shuangchuan Team” Program, Key Laboratory of Advanced Photonic and Electronic Materials, Collaborative Innovation Center of Solid-State Lighting and Energy-Saving Electronics, and the Fundamental Research Funds for the Central Universities, China.

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