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A facile covalent strategy for ultrafast negative photoconductance hybrid graphene/porphyrin-based photodetector

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Abstract

As a powerful complement to positive photoconductance (PPC), negative photoconductance (NPC) holds great potential for photodetector. However, the slow response of NPC relative to PPC devices limits their integration. Here, we propose a facile covalent strategy for an ultrafast NPC hybrid 2D photodetector. Our transistor-based graphene/porphyrin model device with a rise time of 0.2 ms and decay time of 0.3 ms has the fastest response time in the so far reported NPC hybrid photodetectors, which is attributed to efficient photogenerated charge transport and transfer. Both the photosensitive porphyrin with an electron-rich and large rigid structure and the built-in graphene frame with high carrier mobility are prone to the photogenerated charge transport. Especially, the intramolecular donor-acceptor system formed by graphene and porphyrin through covalent bonding promotes photoinduced charge transfer. This covalent strategy can be applied to other nanosystems for high-performance NPC hybrid photodetector.

Supplementary material for this article is available online

Keywords: 2D material, photodetector, covalent strategy, ultrafast response time, negative photoconductance

(Some figures may appear in colour only in the online journal)

1. Introduction

Photodetectors have a wide range of applications in spectroscopy, telecommunication, astronomy, pharmaceuticals and environmental monitoring [1–6]. Exposure of semiconductors to light with energy larger than band gap generates excess mobile charges (electrons or holes) in the conduction or valence bands and leads to an increase or decrease in electrical conductivity of the semiconductors, it can be divided into two types: positive photoconductance

(PPC) or negative photoconductance (NPC) [7]. And the PPC effect is commonly observed for most photodetectors. As a powerful complement to PPC, NPC as an effect of a reduced conductivity under light illumination, holds great potential for photodetector. For instance, a photoelectric logic gate can be designed by combining PPC and NPC [8, 9].

For the devices with the PPC effect, the response time can be as low as several microseconds [10], while the reported fastest response time of the NPC devices is in the range of milliseconds [11]. This mismatch of response time limits integration of the two effects. To bridge this gap, researchers have explored different methods for material

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preparation. The NPC effect has been found only in a few low-dimension single materials, such as InAs and Si nanowires, monolayer MoS₂, InN thin film, and few-layer graphene (Gr) [11-15]. And the harsh preparation conditions of ultra-low temperature and ultra-vacuum dramatically hinder the application of single materials. So far, preparation of hybrid NPC nanomaterials by design of band structures has been the focus of NPC photodectors. For example, ZnO quantum dots were encapsulated into SiO2 with the photoresponse rise time of 12 h and decay time of 20 min [16]. Then, the van der Waals (vdW) heterojunction structure has been adopted to fabricate NPC photodetector [7]. In recent years, the Gr-based devices [17-20], such as CsPbBr₃/Gr [21] and Au nano particles modified reduced graphene oxide [22] have attracted intense attention thanks to the unique zero bandgap and especially the high carrier mobility of Gr. Among them, the Au/Gr/p-type Si heterojunction has the rise time of 0.4 ms and the decay time of 0.5 ms under high light intensity based on the photobolometric effect [19], which is the fastest response time in the reported NPC hybrid photodetectors. However, the response time still needs to be further improved. Otherwise, usage of noble metals might increase the cost.

Monolayer Gr is a promising material for photodetector applications owing to its conductivity, ultrahigh mobility and stability, which are ideal properties for high-speed photodetection [23–25]. However, the light absorption of monolayer Gr is very weak because of its ultrathin structure and zero band gap. The photoresponsivity of pure Gr photodetector is ultralow ($\sim 10^{-3}$ A W⁻¹) [26]. To address these problems, Transition metal disulfides (WS₂) [27], quantum dots (PbS) [28], organic semiconductors (organic dye) [29, 30], and inorganic-organic materials (perovskite) [31] have been combined with Gr to enhance light absorption. In comparison with the other materials, organic-Gr hybrid films can be fabricated easily through a simple solution process over large areas, which have attracted intense interest from researchers [24].

Porphyrins as planar, electron-rich organic dye molecules, characterized by remarkably high extinction coefficients in the visible region [32]. However, the development of an effective strategy to enhance the electron transfer rate still remains a challenge. Porphyrin fluorescence was recently found to undergo strong quenching upon interaction with Gr [33]. These two materials combine and create a donor (D)– acceptor (A) system, which can be used for energy conversion applications.

Hybrid nanostructures, which combine the unique properties of individual constituents, exhibiting optimized performance [24, 34]. Gr can be combined with organic dye molecules by covalent or non-covalent methods. In contrast to non-covalent methods, covalent functionalization may result in conjugation via a π -delocalizable linkage that can facilitate their further optoelectronic application [35]. The covalent functionalization reactions of Gr include two general routes. One is the covalent functionalization of Gr sp² carbon networks (cycloadditions, free-radical additions, and click reactions), and the other one is the use of oxygen-containing groups on Gr (cycloaddition reaction, amidation reaction and esterfication reaction).

Herein, we propose a facile covalent strategy for an ultrafast NPC hybrid transistor-based 2D photodetector. The low-cost Gr and 5, 10, 15, 20-tetracarboxylic (4-aminophenyl) porphyrin (TAPP) are chosen as the model materials because, similar to Gr, the photosensitive porphyrin also has an electron-rich and large rigid structure, which is prone to the photogenerated charge transport. More importantly, the intramolecular D-A system, formed by porphyrin and Gr by the stable covalent bond, not only enhances the structural stability but also facilitates the photogenerated electron transfer at the D-A interface, compared to the non-covalent strategies. Thus, our Gr/porphyrin device with the rise time of 0.2 ms and the decay time of 0.3 ms has the fastest response time in the so far reported NPC hybrid photodetectors. This strategy can be applied to other nanosystems to further improve the performance of NPC hybrid photodetector.

2. Experimental section

2.1. Photodetector preparation

The monolayer Gr grown on the copper foil was purchased from Shanghai Onway Technology Co., Ltd., that is more convenient to use than multilayer graphene. The thin poly (methyl methacrylate) (PMMA) as a mechanical support layer was first spin-coated on the surface of the Gr at 1000 rpm for 30 s, and baked at 120 °C for 5 min. Next the PMMA/Gr/Cu material and platinum foil as the cathode and anode respectively were immersed in 1 mol 1^{-1} NaOH solution, and applied an electrolysis voltage of 2.25 V. After the PMMA/ Gr film was completely separated from the Cu foil through electrochemical bubbling [36], the film was picked up and rinsed carefully in deionized water in order to remove electrolyte residues. Afterward, the PMMA/Gr film was transferred onto the heavily-doped n-type Si substrate covered with a 300 nm SiO₂ layer, and then baked in a vacuum oven at 80 °C for 30 min to expel the remaining H₂O and improve adhesion between Gr and substrate, followed by removing the PMMA layer in acetone to get the as-transferred Gr sample. Subsequently, the Gr sample was treated by O_2 plasma for the optimized 5 s at the power of 10 W to obtain the plasma treated Gr (PT-Gr) with active sites. After that, the PT-Gr sample was dipped in the 1,3-dicyclohexylcarbodiimide and 4-dimethylaminopyridine mixed solution (DCC-DMAP, 1 mmol 1^{-1}) at room temperature for 30 min to achieve carboxyl activation of Gr. Then, the sample was transferred into the TAPP solution (1 mmol l^{-1}) and reacted for 48 h at room temperature to obtain the PT-Gr/TAPP sample, followed by washing three times with N, N-dimethylformamide (DMF) and N_2 blow drying. Finally, the Cr/Au (3 nm/40 nm) metal electrodes of the PT-Gr/TAPP device were deposited by thermal evaporation with a copper grid of Transmission Electron Microscope (GVSH, Gilder grid, UK) as the shadow mask.



Figure 1. (a) The synthetic procedure for PT-Gr/TAPP (the Si/SiO₂ substrate was omitted for clarity), (b) schematic diagram of the PT-Gr/TAPP transistor-based 2D photodetector.

2.2. Characterization

Raman spectra were acquired using a Renishaw inVia plus system with a 514 nm wavelength laser in an ambient environment. The x-ray photoelectron spectroscopy (XPS) spectra were characterized by Ulvac-PHI Quantera II. Atomic force microscopy (AFM) spectra were obtained by Tastlab-Multimode (Multimode picoforce). SEM spectrum was obtained by SU8220 (Hitachi-SU8220) with an operating voltage of 7 kV. The Fluorescence spectra were characterized by FluoroMax (FluoroMax Plus). The light sources were set up using dot lasers (UV LED) with wavelengths of 360, 420 and 532 nm. The electrical characteristics were measured by a PDA FS-Pro semiconductor parameter analyzer with a probe station. The Fluorescence spectra were characterized by FluoroMax (FluoroMax Plus).

3. Result and discussion

The Gr monolayer on the Si/SiO₂ was treated by O₂ plasma to obtain the p-type plasma treated Gr (PT-Gr). Compared to the commonly used strong oxidizing agents, the degree of Gr oxidation is more controllable and environmentally friendly by O₂ plasma treatment [37]. Then, the PT-Gr sample was dipped in the DCC-DMAP mixed solution (DCC-DMAP) to achieve carboxyl activation of Gr. After that, the sample was transferred into the TAPP solution, where carboxyl groups of Gr and TAPP were bonded together through amidation reaction to obtain the PT-Gr/TAPP sample (figure 1(a)). Our single-layer PT-Gr reacting on the surface of SiO₂ can be easily cleaned, avoiding the disturbance of residues on the device performance; while the Gr oxide powders dispersed in the solution are liable to aggregate, which is difficult to wash.

Noted that we investigated the effect of O_2 plasma treatment on the structure of Gr by Raman spectroscopy and XPS in the process of device fabrication. As shown in figure 2(a), the Raman spectra of investigated samples display a *D* peak at 1359 cm⁻¹, a signature of structural disorder in Gr, and a *G* peak at 1600 cm⁻¹, in-plane stretching vibrations of sp²-hybridized carbon atoms, respectively. The intensity ratio of the D band to



Figure 2. (a) Raman spectra of Gr on the Si/SiO₂ wafer as a function of O₂ plasma treatment time, obtained at $\lambda_{exc} = 514$ nm, (b) XPS spectra of C1s of the Gr and PT-Gr/TAPP (5 s).

the G band (I_D/I_G) is generally considered a qualitative indicator of the defect density in Gr layer [38]. The I_D/I_G ratio ranges from 0.19 to 2.11, when the treatment time changes from 0 to 7 s. It suggests that O₂ plasma modification could increase the disorder of Gr as well as the percentage of oxygen functional groups with increasing treatment time. The 2D band, located at about 2695 cm⁻¹, which is the overtone of the D band. Its intensity is sensitive to the presence of structural disorder, i.e. it tends to decrease in the presence of large amounts of disorder [39]. As the O₂ plasma treatment time increases, the 2D peak intensity gradually decreases. Especially, the 2D peak dramatically weakens at the 7 s, denoting a large amount of structural defects in its carbon lattice, which will seriously affect the electrical properties of Gr, the peak intensity ratios I_{2D}/I_G is extracted (figure S1, supporting information) [40].

The XPS spectra of C1s for Gr and PT-Gr (5s) can be deconvoluted in 5 main peaks, which are usually attributed to 284.4 eV (C=C), 285.0 eV (C-C), 286.3 eV (C-O), 287.2 eV (C=O), and 289.1 (O-C=O) (figure 2(b)) [41]. Comparing the spectra, it is clear that the C1s peak pattern broadens and has a bulge at 289 eV, which indicates that a relative increase in the oxygen group. The percentage of C=C decreased from 69.75% in Gr to 28.67% in PT-Gr, while the C-C peak increased from



Figure 3. (a) Raman spectra of PT-Gr (black), PT-Gr/TAPP (red) and TAPP (green), obtained at $\lambda_{exc} = 514$ nm, (b) XPS spectra of PT-Gr (black) and PT-Gr/TAPP (red), (c) C1s and (d) N1s spectra of PT-Gr/TAPP.

16.12% to 46.46%. This also happened with C=O, which increased from 0.98% to 3.51%, and O–C=O, which changed from 3.06% to 11.07%, indicating that the degree of oxidation in Gr increases after O_2 plasma treatment, which is conducive to the amidation reaction. Therefore, the PT-Gr (5 s) sample is selected for the next reaction, which has rich active sites (–COOH groups) and avoids serious structural damage.

Then, the composition of PT-Gr/TAPP was elucidated from the Raman spectra (figure 3(a)), together with PT-Gr, and TAPP for comparison. Same as PT-Gr, PT-Gr/TAPP shows a *D* peak at 1359 cm⁻¹, and a *G* peak at 1600 cm⁻¹, respectively. The data displays there are lattice defects of Gr and sp² carbon network in these samples. Particularly, the Raman spectrum of PT-Gr/TAPP exhibits the intensity ratio of D to G band increases from 1.37 to 2.14 comparing with PT-Gr. The intensified I_D/I_G can be accounted to more defects produced by modification. Besides, the feature peaks of TAPP at 1236, 1327, 1352, 1452, 1488, and 1543 cm⁻¹ appear in the PT-Gr/TAPP sample, indicating the TAPP constituent is present [42]. The above Raman spectra confirm the existence of the Gr and TAPP components in the PT-Gr/TAPP sample.

XPS analysis was also performed to identify the chemical states and interfacial interaction in PT-Gr/TAPP. Compared with PT-Gr, the additional peak assigned to N1s at around 400 eV can be clearly detected in the spectrum of PT-Gr/TAPP within a wide energy range (figure 3(b)). Combing with the above Raman spectra, the existence of TAPP in PT-Gr/TAPP is further confirmed. By comparing with PT-Gr C1s spectrum (figure 2(b)), the C1s peak pattern broadens and has a bulge at 287 eV the percentage of C=C decreased from 28.67% to 18.09% in PT-Gr/TAPP, while the C-C peak decreased from 46.46% to 37.09%. More importantly, the percentage of C=O in PT-Gr/TAPP C1s spectrum is significantly increased from 3.51% in PT-Gr to 24.87% and the intensity of O-C=O decreased from 11.07% in Gr to 4.34% in PT-Gr (figure 3(c)),



Figure 4. Height images measured by AFM of (a) PT-Gr and (b) PT-Gr/TAPP samples over $18 \times 18 \ \mu m^2$ area, the three dimensions AFM images of (c) PT-Gr and (d) PT-Gr/TAPP samples corresponding to the two frames, the height profiles of (e) PT-Gr and (f) PT-Gr/TAPP samples along the four white dashed lines.

which is attributed to the transformation of -COOH groups into -CONH- groups based on the condensation of the -COOH and $-NH_2$ groups on the PT-Gr and of TAPP, respectively [43]. Besides the deconvoluted peaks of N1s centered at C-N (398.9 eV), C-NH (400.2 eV), the peak of O=C-NH (402.1 eV) is caused by the nucleophilic reaction between the amino of TAPP and the carboxyl of PT-Gr for the PT-Gr/TAPP (figure 3(d)) [44, 45]. These XPS spectra demonstrate that PT-Gr is connected with TAPP by the -CONH- covalent bond in the PT-Gr/TAPP sample.

AFM analysis was performed to determine the surface roughness and thickness of PT-Gr/TAPP nanosheets. The root mean square (RMS) roughness of the PT-Gr surface is 1.37 nm. Compared to the PT-Gr sample, the PT-Gr/TAPP sample has a much higher RMS roughness of 4.85 nm. These differences are highlighted in figures 4(c) and (d), where the three dimensions AFM images corresponding to the two frames in figures 4(a) and (b) are shown. The line-scan height profiles as shown in figure 4(e) and (f), corresponding to the two dashed lines in figures 4(a) and (b). The results give the thickness of the PT-Gr/TAPP sample as 5.53 nm, thicker than the PT-Gr (3.69 nm). These results are in good agreement with the Raman and XPS outcomes. This can be attributed to the introduction of TAPP onto the PT-Gr nanosheet.



Figure 5. SEM image of the PT-Gr/TAPP transistor-based photodetector.

Figure 5 shows the SEM image of the PT-Gr/TAPP transistor-based photodetector. The Cr/Au metal electrode film is compact, smooth, uniform and cracks free, and the channel lengths of the photodetector is \sim 15 μ m.

In order to accurately test the photoresponse properties of the PT-Gr/TAPP photodetector, a series of measurements were carried out, including the spectral selectivity, response time and responsivity. First, we explored the spectral selectivity of the PT-Gr/TAPP photodetector. The UV-vis absorption spectroscopy of TAPP in DMF was performed in order to measure the spectral response range of TAPP. The spectrum of TAPP exhibits a strong Soret absorption at 435 nm, and weak Q-bands between 500 and 700 nm, which are consistent with that of other porphyrins analogues (figure 6(a)) [46, 47]. This result indicates the PT-Gr/TAPP photodetector has significant photoresponse at the wavelength of about 435 nm. Figure 6(b) shows the photoelectric response of the PT-Gr/TAPP photodetector under chopped illumination with different wavelengths. We use the UV LED point light as the signal source, which switching time is in the nanosecond range. The light is switched on and off periodically at 20 s intervals, and the corresponding chopping frequency is 0.025 Hz. A precision source/measurement unit (PDA FS-Pro semiconductor parameter analyzer) is used signal acquisition and the setting sampling rate is 10 MHz. Results shows that the current obtained from the PT-Gr/TAPP photodetector under the illumination of 532 and 360 nm are almost the same as the dark current. While the current is lower under the 420 nm laser illumination than the dark current. This result shows that the PT-Gr/TAPP photodetector has obvious NPC photoelectric response under 420 nm laser illumination. The response turns out to be very stable and repeatable over multiple cycles.

Next, we examine the response time, a parameter that describes how fast a photodetector responds to a step-in input light signal of the PT-Gr/TAPP photodetector by the test of transient photocurrent response. The response time includes the rise time (τ_r) and the decay time (τ_f), defined as the

corresponding time required when the photocurrent increases from 10% to 90% and decreases from 90% to 10% respectively [6]. The chopping frequency and the setting sampling rate are the same as in the spectral selectivity test. The τ_r of 0.2 ms and the τ_f of 0.3 ms are recorded from the transient photocurrent curve of the PT-Gr/TAPP photodetector (figure 6(c)). Its response time is the fastest among the NPC hybrid photodetectors reported to date (table 1).

Figure 6(d) shows the transfer characteristic curves of the PT-Gr/TAPP photodetector. The charge neutrality points of the curves are located at the positive source-gate voltages (V_{gs}) both in dark and under illumination with 420 nm, indicating the PT-Gr/TAPP is a p-type semiconductor material [54]. The charge neutrality point at 20 V shows a negative V_{gs} direction shift under illumination comparing with that at 70 V in dark, and the source-drain current (I_{ds}) under illumination is lower than that in dark at the V_{gs} below about 50 V, demonstrating an NPC effect of the device. The NPC effect is more obvious in the I_{ds} - V_{ds} output curves at the zero applied gate voltage, since all the currents of the PT-Gr/TAPP device under 420 nm illumination with different light power are lower comparing with that in dark (figure 6(e)).

To further explore transfer characteristic of the device, the photocurrent (I_{ph}) curves are extracted from the I_{ds} - V_{ds} output curves under illumination with different light power and in the dark, following the calculation formula below:

$$I_{ph} = I_{\text{light}} - I_{\text{dark}},\tag{1}$$

where I_{light} and I_{dark} represent the illumination and dark current, respectively. At $V_{ds} = 1$ V, the photocurrent ranges from -1.16 to -2.47 mA for a light power from 14.8 to 74.0 μ W (figure 6(f)). It makes clear that when the source-drain voltage is constant ($V_{ds} = 1$ V), the photocurrent directly depends on the light power intensity and increases with increasing light power.

The responsivity (R) of the photodetector, representing the amount of signal current generated for per unit power of a specific wavelength radiation, is also calculated by equation (2) as follows:

$$R = \frac{I_{ph}}{P},\tag{2}$$

where *P* is the light power. As revealed in figure 6(f), the photoresponsivity of the PT-Gr/TAPP device ranges from -78.4 to -33.2 A W⁻¹, when the light power changes from 14.8 to 74.0 μ W. The responsivity of the device significantly decreases with increasing light power. In this work, the highest responsivity of 78.4 A W⁻¹ was obtained at a low light power of 14.8 μ W.

In order to estimate the noise level of the device, Fourier transform was performed to the dark current (figure S2, supporting information), and we extracted the root mean squared noise current ($N_{\rm rms}$) at the detection bandwidth of 1 Hz [31, 55, 56]. Then The electrical signal-to-noise ratio (SNR) is calculated according to the following formula:

$$SNR = \frac{I_{ph}}{N_{rms}}.$$
 (3)



Figure 6. (a) The UV–vis absorption spectrum of TAPP in DMF, (b) time response of the PT-Gr/TAPP photodetector under irradiation with 420, 360 and 532 nm wavelength, (c) transient photocurrent response of the PT-Gr/TAPP photodetector, (d) the I_{ds} - V_{gs} transfer curves of the PT-Gr/TAPP photodetector under the illumination intensity of 74 μ W, (e) the I_{ds} - V_{ds} output curves under illumination with different light power, (f) light-power-dependent photocurrent and photoresponsivity at $V_{ds} = 1$ V, $V_{gs} = 0$ V.

As a result, we obtained a SNR of about 841, when the light power is 14.8 μ W, which the I_{ph} is -1.16 mA. We collected the SNR valuess for Gr-based photodetectors in recent years, as shown in table S1. The SNR of the photodetector calculated by the Formula (3), is related to the power of the light signal. Because the light power in our work is inconsistent with those in literature, therefore, our SNR cannot be strictly compared with others here. It might only be used as a rough reference.

In order to analyze the NPC response mechanism of the PT-Gr/TAPP device under illumination, photoluminescence spectroscopy was employed to investigate the electronic interactions between the PT-Gr and TAPP component. Upon excitation at 460 nm, the fluorescence emission peak of the PT-Gr/TAPP at 667 nm shows a blue shift about 15 nm relative to that the TAPP at 682 nm, and the fluorescence emission intensity of the PT-Gr/TAPP distinctly increases compared to that the PT-Gr sample (figure 7(a)). These changes might be attributed to the effective photoinduced electrons transfer from the TAPP units to the PT-Gr sheet in the excited state [33, 57]. This deduction can also be corroborated by the shift of the charge neutral point of the PT-Gr/ TAPP photodetector to the negative gate voltage under illumination (figure 6(d)). Based on the above discussions, we analyze the underlying mechanism for the ultra-fast NPC response of the PT-Gr/TAPP photodetector (figure 7(b)). The intramolecular D-A system forms by coupling the PT-Gr electron acceptor with the electron donor TAPP by the -CONH- covalent bond. When light is illuminated on the PT-Gr/TAPP photodetector, electron-hole pairs are first generated in the photosensitive TAPP units. Then, the photogenerated electrons in the lowest unoccupied molecular orbital (LUMO) of the electron donor TAPP are transferred to the PT-Gr electron acceptor, and accordingly the Fermi level of the p-type PT-Gr moves up with injection of the photogenerated electrons. This is confirmed by the shift of the charge neutral point of the PT-Gr/TAPP photodetector to the negative gate voltage under illumination. For a p-type semiconductor, the hole concentration determines conductivity [21]. The effective photoinduced electrons decrease the hole concentration in the PT-Gr, resulting in the decreased current in the PT-Gr/TAPP photodetector compared to that in dark, that is, the NPC effect.

The Gr-based devices have attracted intense attention thanks to the unique zero bandgap and especially the high carrier mobility of Gr, which are ideal properties for highspeed photodetection. The photosensitive porphyrin has an electron-rich and large rigid structure, which is prone to the photogenerated charge transport. As an effective strategy, covalent bonding between TAPP and PT-Gr facilitates the photogenerated electrons transfer at this intramolecular D-A interface together with the excellent carrier transport property in each component, which contributes to the ultrafast NPC photoresponse of the PT-Gr/TAPP photodetector.

The τ_r of 0.2 ms and the τ_f of 0.3 ms are recorded from the transient photocurrent curve of the PT-Gr/TAPP photodetector (figure 6(c)). The reason of τ_r is shorter than τ_f is proposed that the response of the PT-Gr/TAPP to light is two Response

Table 1. Summary of NPC hybrid photodetectors.

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Material	range	Preparation method	Response time (ms)		W^{-1})	Year	References
			$ au_{ m r}$	$ au_{\mathrm{f}}$			
PT-Gr/TAPP	420 nm	chemical	0.2	0.3	-78.4		This work
		functionalization					
ZnO NPs/SiO ₂	UV	physical mixture	7.2×10^{5}	2.8×10^5	—	2009	[16]
rGO/Au NPs	532 nm	physical mixture	8.4×10^4	5.8×10^4	-10.05	2017	[22]
rGO/SnO ₂ NPs	365 nm	physical mixture	440	240	—	2015	[23]
rGO/MoO ₃	650 nm	physical mixture	5.0×10^{5}	1.0×10^4	—	2014	[48]
$BP/SnS_{0.5}Se_{1.5}$	UV	vdW heterojunction	—		-450	2019	[49]
$MoS_2/h-BN/ReS_2$	Vis	vdW heterojunction				2020	[7]
Gr/Rhodamine/Gr	520 nm	vdW heterojunction	10^{4}	10^{4}	-10^{3}	2019	[17]
MoSe ₂ /Gr	550 nm	vdW heterojunction	—	2×10^4	—	2019	[18]
Au/Gr/p-Si	Vis- IR	vdW heterojunction	0.5	0.4	—	2019	[19]
CsPbBr ₃ /Gr	UV	vdW heterojunction	9.5×10^{5}	5.0×10^4	—	2021	[21]
WS ₂ NSs/Au NPs	Vis	vdW heterojunction	1.8×10^4	3.7×10^{5}	—	2018	[50]
Gr/MoS_2	635 nm	vdW heterojunction	—	8.0×10^{3}	-5×10^8	2013	[51]
rGO/WS_2	808 nm	vdW heterojunction	3.6×10^{4}	5.4×10^{4}	6	2014	[52]
BP/Gr	655 nm	vdW heterojunction	—		—	2018	[53]

BP: black phosphorus, NS: nanosheet, UV: ultraviolet, Vis: visible, IR: infrared, τ_{t} : rise time, τ_{t} : decay time.



Figure 7. (a) Fluorescence emission spectra of the PT-Gr/TAPP, TAPP and PT-Gr samples, obtained at $\lambda_{\text{exc}} = 460$ nm, (b) the energy band diagrams of the PT-Gr/TAPP device with and without light illumination.

complex paths of electron-hole pairs generation, transfer and recombination; while only one recombination path is involved between electrons in Gr and holes in TAPP [58]. Specifically, the photogenerated electrons in TAPP units have two competitive recombination paths when light is on: one is recombination with photogenerated holes in TAPP, and the other is to recombine with holes in Gr after transferring to Gr due to the molecular polarization in this D-A system, which can be regarded as a micro built-in field. By contrast, a direct fast carrier recombination results in a quick recovery of hole density and conductance in Gr of the D-A system when the light is off. The responsivity of the device significantly decreases with increasing light power (figure 6(f)). It is attributed to the photogating effect, in which photogenerated electrons or holes are trapped in trapping centers, and the charged trapped states can act as a locally floating gate and modulate channel conductivity [59-61]. This effect involves complex processes of carrier generation, trapping, and recombination. When light is incident on the device, photogenerated electron-hole pairs are first generated in TAPP. Then, photogenerated electrons flow into Gr due to the builtin field in this D-A system, and photogenerated holes remain in TAPP. Accumulation of photogenerated holes in the TAPP units can result in a reversed electric field with a direction opposite to that of the intrinsic built-in field. Therefore, the net built-in field becomes weaker under higher incident light powers and fewer photogenerated electron-hole pairs will be separated, leading to a reduction in the responsivity with increasing light power. With adding concentration of the photogenerated carrier in TAPP units at the higher power density, the increase in the photogenerated carrier recombination rate in the photosensitive TAPP units also reduces the responsivity of the device as the light power enhances [58, 62].

4. Conclusion

In summary, we developed a facile and effective covalent strategy for an ultrafast NPC hybrid 2D photodetector. Our Gr /porphyrin device has the fastest response time in the so far reported NPC hybrid photodetectors. It is attributed to efficient photogenerated charge transport and transfer of the material. Both the photosensitive porphyrin with an electronrich and large rigid structure and the built-in Gr frame with high carrier mobility are prone to the photogenerated charge transport. More importantly, the intramolecular D-A system formed by Gr and porphyrin through covalent bonding promotes photoinduced charge transfer. This covalent strategy is applicable in other nanosystems to further improve the performance of NPC hybrid photodetector.

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Data availability statement

The data generated and/or analysed during the current study are not publicly available for legal/ethical reasons but are available from the corresponding author on reasonable request.

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