ADVANCED ELECTRONIC MATERIALS

Supporting Information

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Efficient Photodoping of Graphene in Perovskite–Graphene Heterostructure

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1. Published data sources used for the carrier density calculations

References are as in the main text: Lee [Ref. 6] Figure 3(a); Wang [Ref. 7] Figure 2(b) and 3(b); Spina [Ref. 8] Figure S5; Xie [Ref. 9] Figure S4(a) (for the hole doping regime).

2. Responsivity normalization

The original definition of responsivity used in conventional photodiodes is given by R = $\eta e/\hbar\omega$, where η is the external quantum efficiency (EQE) and $\hbar\omega$ is the incident photon energy, which is equal to R = I_{ph}/P_{in}, where P_{in} is the incident power, when integrated over time and surface area. This formalism is also correct for the solar cells. However, its direct application to the graphene-based phototransistors does not correctly reflect the photocurrent generation efficiency since the auto-normalization to the surface area does not hold for I_{ph}/P_{in} in the phototransistors with effectively 2D channel. This is because the drain current I_d collected from a 2D channel is the surface current density K integrated along the channel width W ($I_d^{(2D)}$ = KW), in contrast to the volume current density j integrated over the cross-section area WL ($I_d^{(3D)}$ = jWL) of the bulk photo-active layer.

For the 2D channel, the Ohm's law gives the photocurrent $I_{ph} = e\Delta p\mu V_{sd}W/L$, and the incident power at the channel is P_{in} = FWL. Then, the responsivity is given by

$$R = \frac{I_{ph}}{P_{in}} = \frac{e\Delta p\mu V_{sd}}{FL^2}.$$

Among all parameters in the equation above, the constants V_{sd} and L are irrelevant to the carrier generation and transport (i.e. the external parameters), and vary greatly between devices. Therefore, the external parameters in the equation represent the normalization factors $V_{sd}W/L$ for the photocurrent, and V_{sd}/L^2 for the responsivity, as shown in Figure S1(a). In other words, the normalization performed for any chosen pair of parameters V_{sd} and L gives the responsivity of the FET with same V_{sd} and L as the reference device. This allows us properly compare the performance of different devices between each other. We calculate the normalization factor for each study based on the published data, as summarized in Table S1, and obtain the normalized responsivity as a function of the incident power density. Figure S1(b) and (c) show the responsivity before (as reported) and after the normalization R_{norm} = R/Norm, respectively. As evident from the plots, the responsivity calculated from as-measured photocurrent and power (Figure S1(b)) do not adequately reflect the performance of the devices, since normalization for the external parameters shifts the data by orders of magnitude in some cases (Figure S1(c)). We conclude that the responsivity is an ambiguous figure of merit for the FET devices with a 2D channel, and the graphene-based photodetectors in particular.

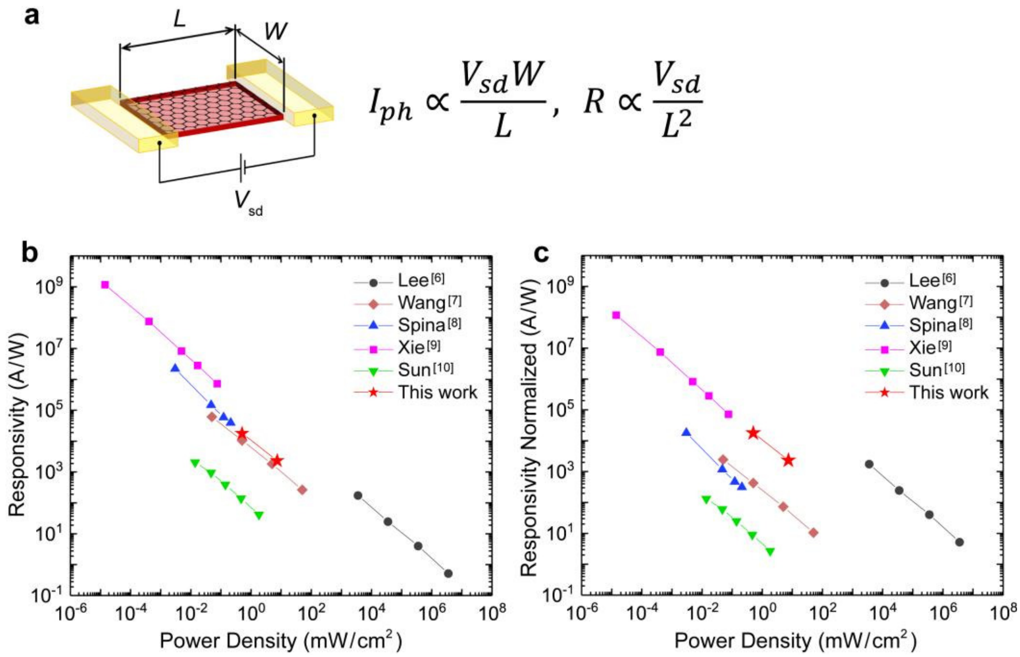

Figure S1. (a) Normalization parameter for the responsivity in the phototransistors with 2D channel. (b) Responsivity of the devices as reported by previous works (calculated as the ratio between measured photocurrent and power). (c) Normalized responsivity of the devises with the same V_{sd} and L as in this work.

Reference	Structure	L, µm	V_{sd}, V	V_{sd}/L^2 ($\times10^{-4}$)	*Norm*
Lee [6]	gr. / $MAPbI_3$	50	0.1	0.4	0.1
Wang [7]	gr. / $MAPbBr_2I$	10	1	100	25
Spina [8]	gr. /$MAPbI_3$	10	5	500	125
C.Xie [9]	gr. / P3HT / $MAPbI_3$	5	0.1	40	10
Sun [10]	Au NPs / gr. / $MAPbI_3$	40	10	62.5	15.63
This work	gr. / MoO_3 / PEDOT:PSS / $MAPbI_3$	50	1	4	1

Table S1. Structure, device paramters, and corresponding normalization factor for responsivity for the previous works on graphene-perovskite phototransistors.

3. Photocurrent response time

Our device shows a rather slow time response characteristic of 10 seconds or more as demonstrated in Figure S2. By applying the bi-exponential fit to the photocurrent time response $I_{ph}(t) = I_{dark} + A[exp(t/\tau_1)] + B[exp(t/\tau_2)]$, we can estimate time response components associated with the carriers generation and recombination (τ_1), and trapping process (τ_2), shown in Table S2.

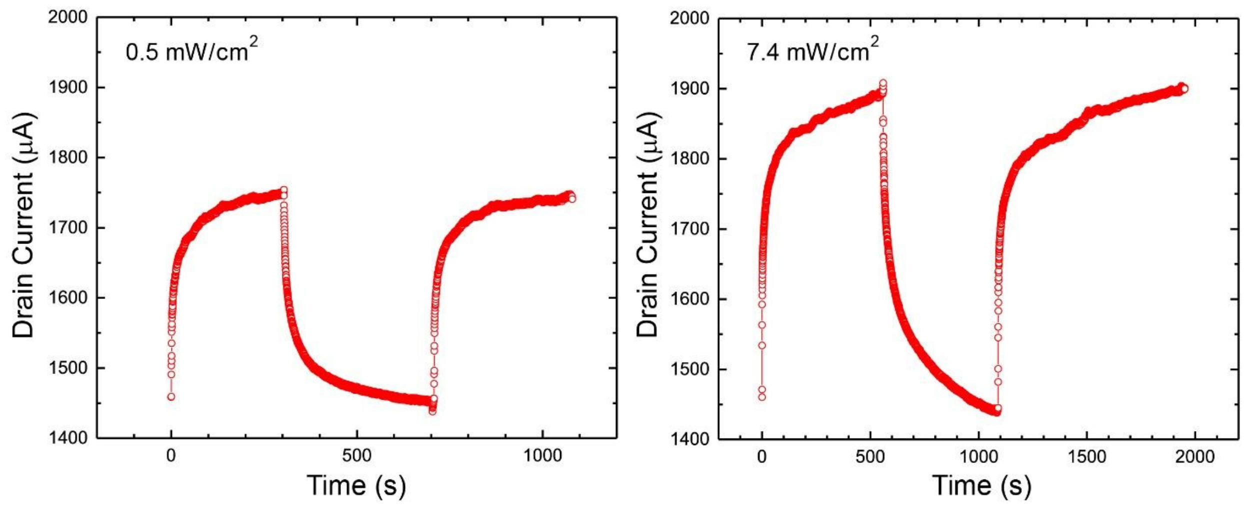

Figure S2. Time response characteristics of our device under different illumination.

	F = 0.5 mW/cm^2		F = 7.4 mW/cm^2	
	Rising time (s)	Falling time (s)	Rising time (s)	Falling time (s)
τ_1	3.4	8.1	12	16
τ_2	71	90	243	195

Table S2. Characteristic time constants of our device under different illumination for 70% of maximum current.

We speculate that the reason for this is that the holes have to pass through the additional transport layers (MoO_3 and PEDOT:PSS), and/or that the perovskite is fabricated in a nano-rod morphology instead of a thin film. We measured the effect of thickness of the PEDOT:PSS layer on the response time as shown in Figure S3. As can be seen, variation of PEDOT:PSS thickness significantly affects photocurrent, and the falling time in particular. Therefore, we can't rule out the leading role of PEDOT:PSS in long response times of our device.

We would like to know that slow photoresponse is the known issue for all graphene-perovskite phototransistors, and is yet to be resolved. The speed of photodoping is, undoubtedly, the next challenge we are facing at in order to realize high-speed all-optical graphene plasmonic modulators. This would involve a careful investigation of the carrier dynamics at layer interfaces and will be discussed in the future works.

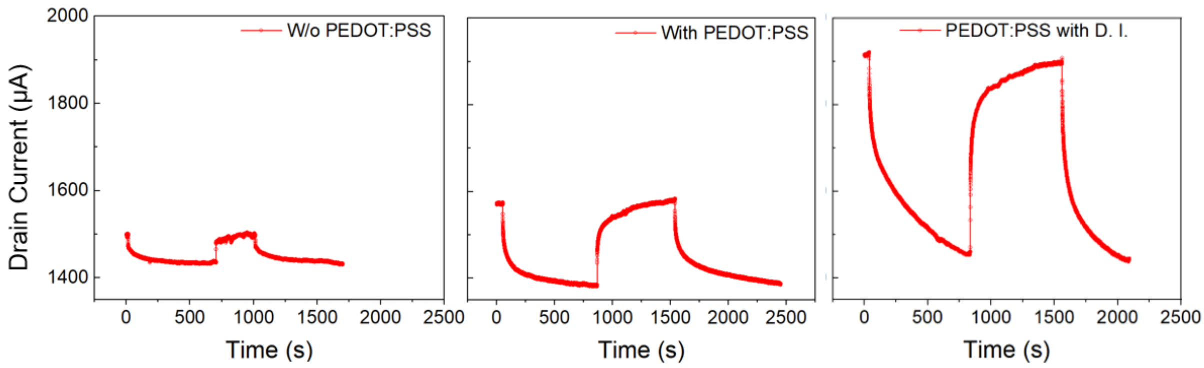

Figure S3. Time response characteristics of our device under F = 7.4 mW/cm^2 for different PEDOT:PSS thickness.