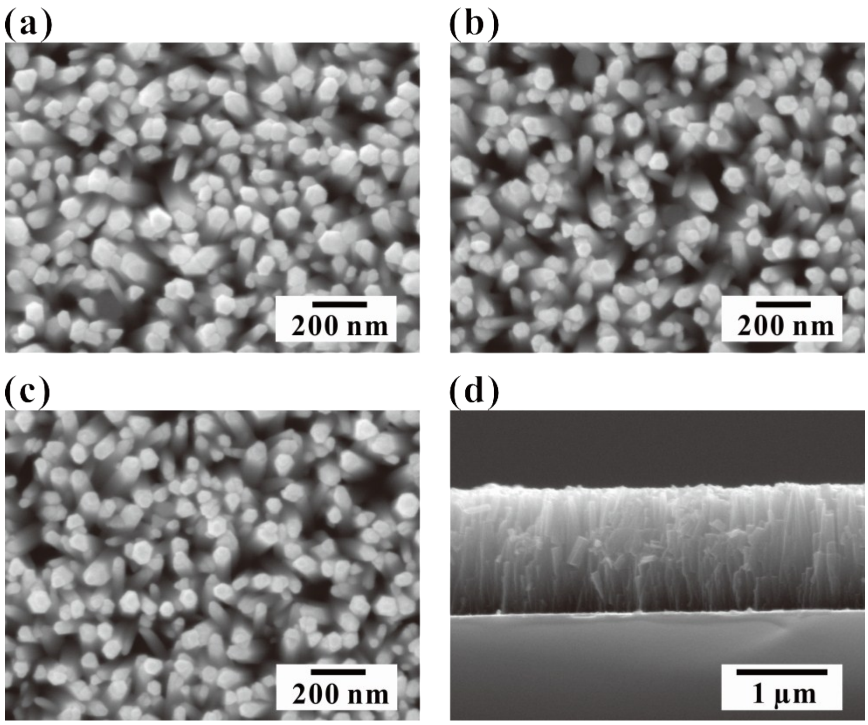

Figure S1. Plane-view SEM image of the (a) pristine ZnO NRs, (b) H:ZnO NRs-350 and (c) ZIF-8@H:ZnO NRs. (d) Cross-sectional SEM image of the ZnO NRs film.

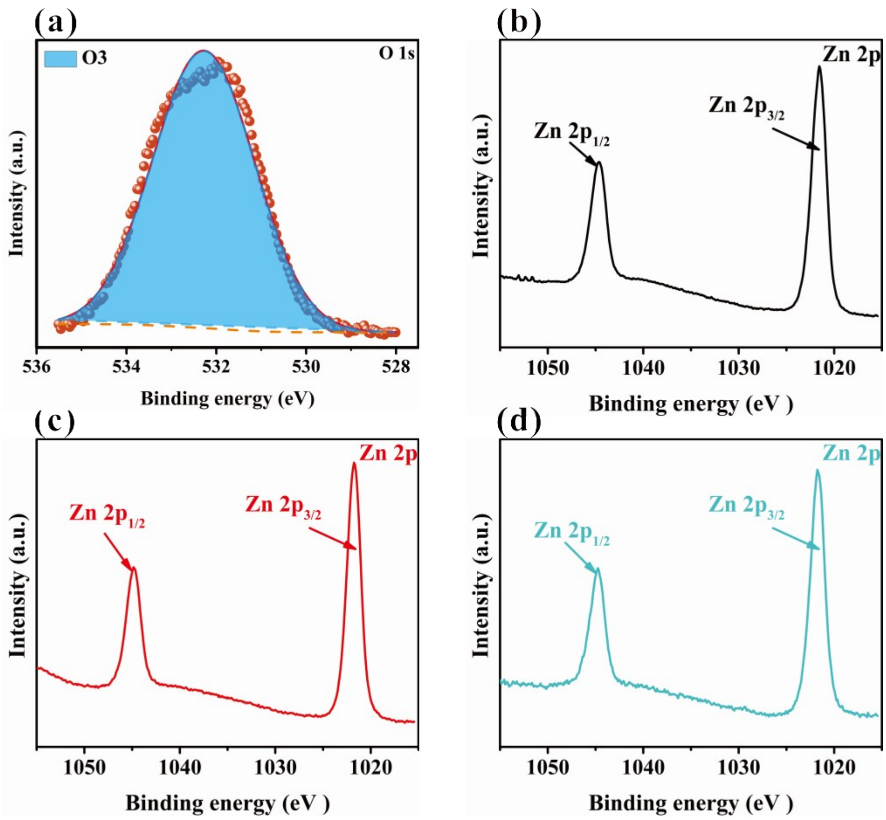

Figure S2. (a) XPS O 1s spectrum of ZIF-8@H:ZnO NRs. XPS Zn 2p spectrum of (b) pristine ZnO NRs, (c) H:ZnO NRs and (d) ZIF-8@H:ZnO NRs.

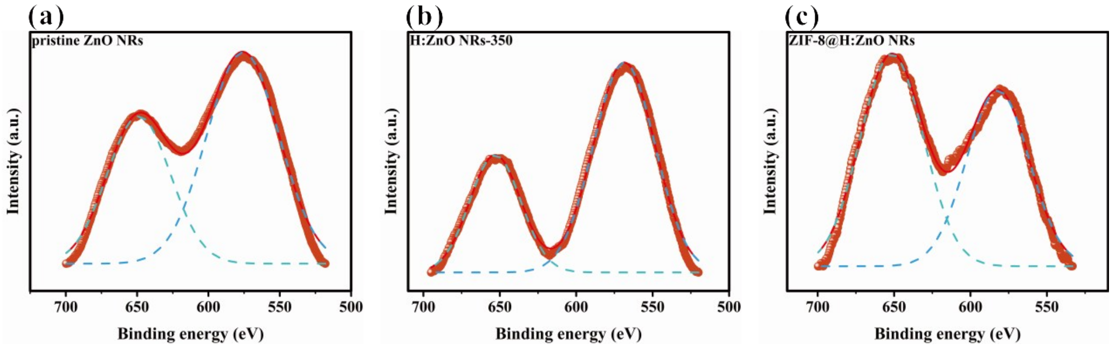

Figure S3. Gaussian distribution fitting curve of the Raman mode centered at (a) ~576 cm^{-1} and ~650 cm^{-1} for pristine ZnO NRs, (b) ~566 cm^{-1} and ~650 cm^{-1} for H:ZnO NRs-350 and (c) ~566 cm^{-1} and ~650 cm^{-1} for ZIF-8@H:ZnO NRs.

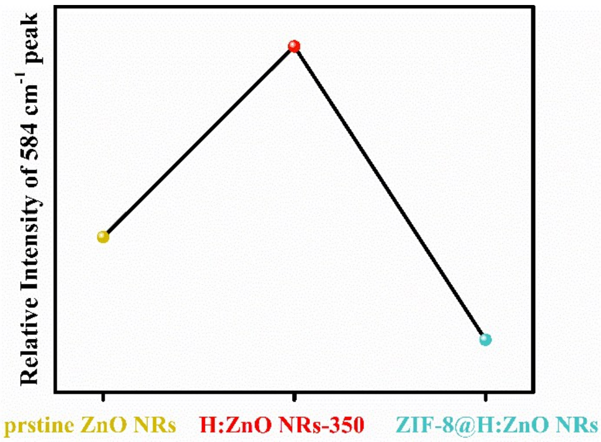

Figure S4. Relative intensity of 584 cm^{-1} peak (oxygen vacancies) for pristine ZnO NRs, H:ZnO NRs-350 and ZIF-8@H:ZnO NRs. Relative intensity can be calculated according to the following equation: Relative intensity for X = the intensity of 584 cm^{-1} peak for X/ the intensity of 579 cm^{-1} peak for X, X = pristine ZnO NRs, H:ZnO NRs-350 and ZIF-8@H:ZnO NRs.

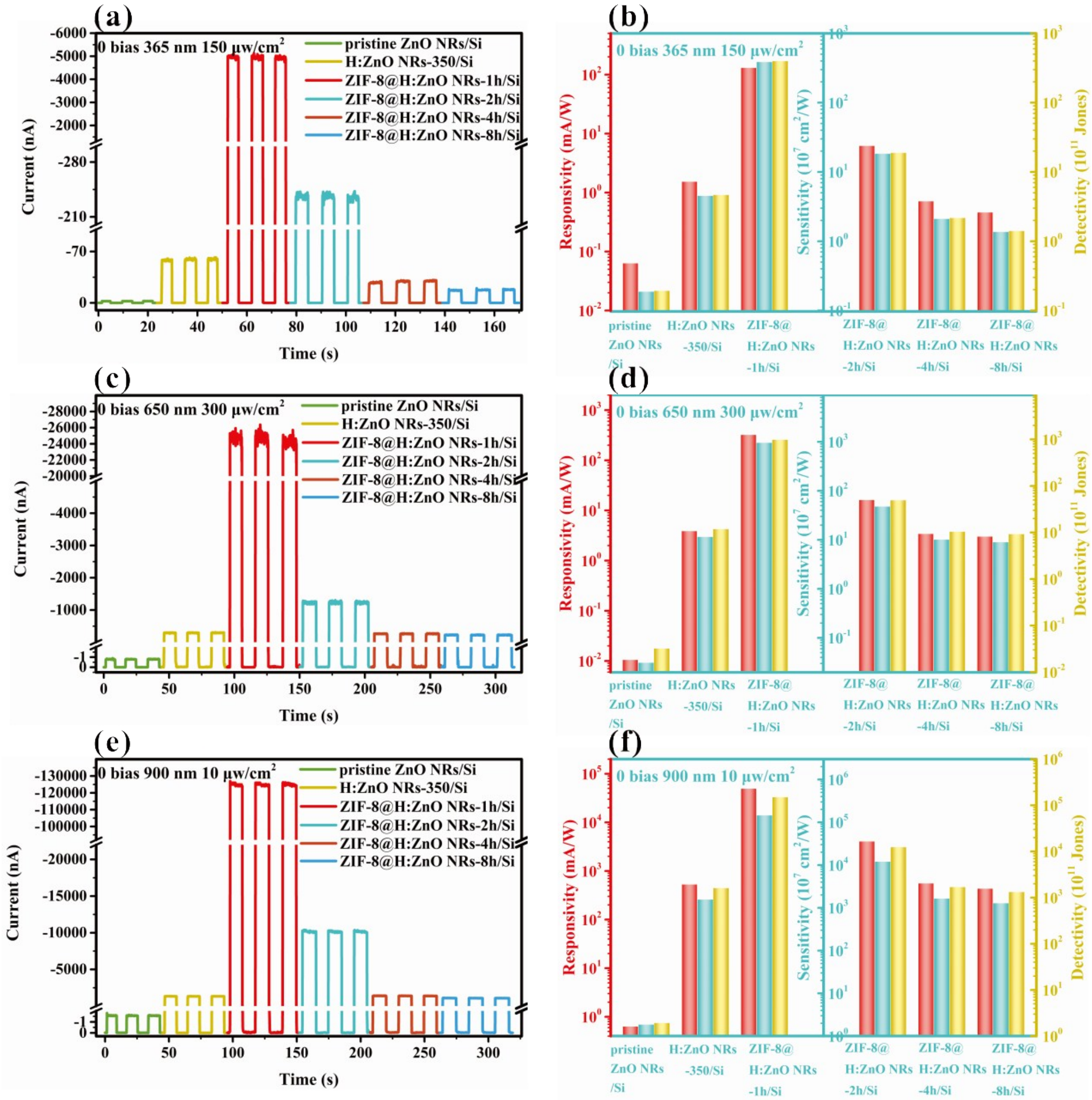

Figure S5. Photocurrent switching performance of the fabricated devices under periodic (a) 365 nm, (c) 650 nm, (e) 900 nm light illumination. External voltages: 0 V. The performance comparison between different devices under (b) 365 nm, (d) 650 nm, (f) 900 nm light illumination. External voltages: 0 V.

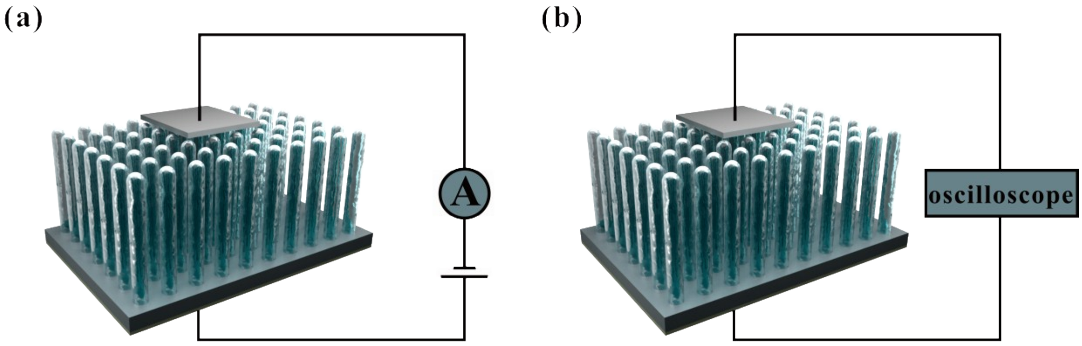

Figure S6. (a) Schematic illustration of the ZIF-8@H:ZnO NRs/*p*-Si heterojunction photodetector. (b) Schematic illustration of measurement circuit for measuring the response time of the device. From top to bottom the device is divided into four layers in order: Pd, ZIF-8@H:ZnO NRs, *p*-Si and In.

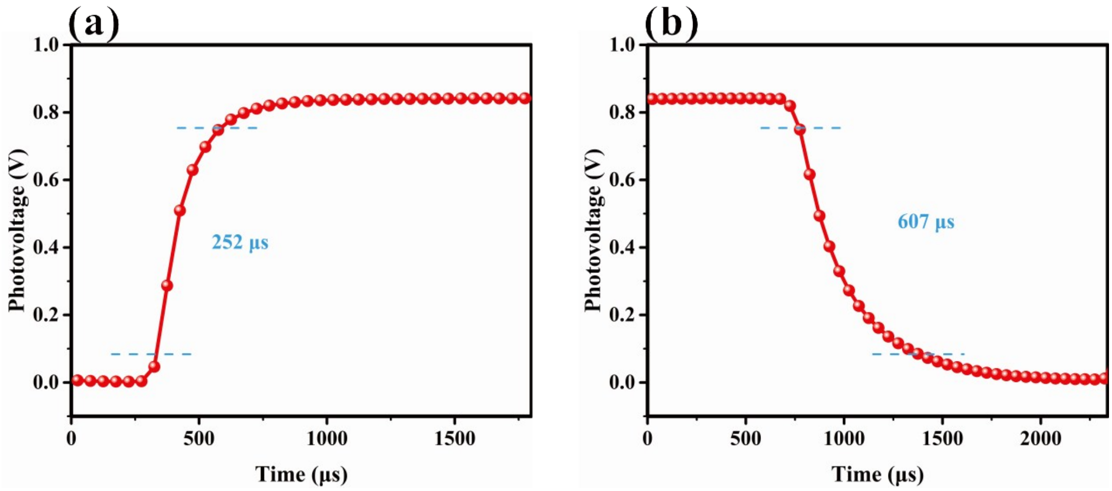

Figure S7. The (a) rise and (b) fall edge, respectively, of the ZIF-8@H:ZnO NRs/*p*-Si heterojunction photoresponse curve.

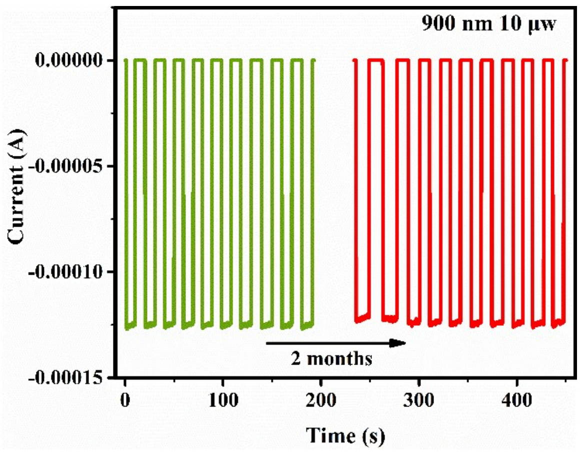

Figure S8. Photoresponse of the photodetector measured before and after storing in the air for 2 months under 900 nm light illumination.

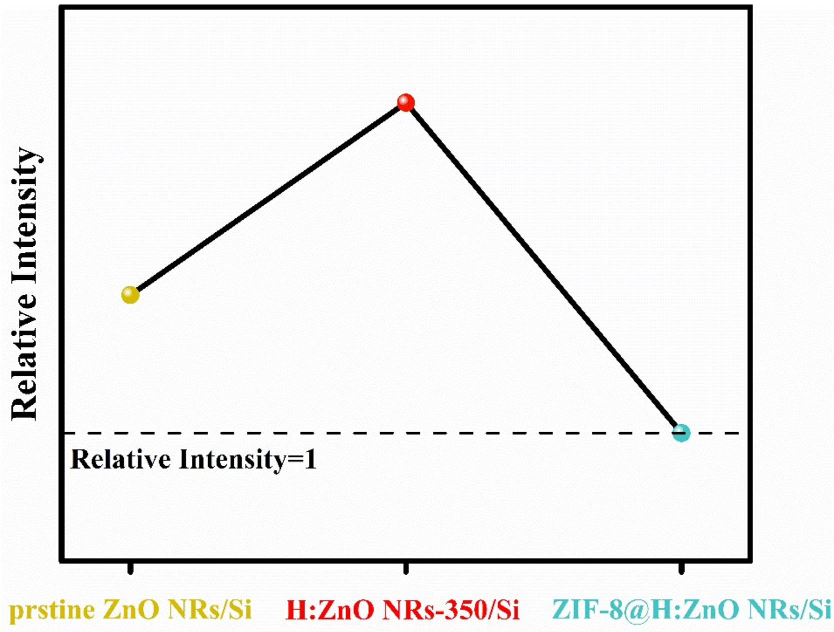

Figure S9. Relative intensity of EPR signal for pristine ZnO NRs/Si, H:ZnO NRs-350/Si and ZIF-8@H:ZnO NRs/Si. (Relative intensity can be calculated according to the following equation: Relative intensity for X = the intensity for X/the intensity for ZIF-8@H:ZnO NRs/Si, X = pristine ZnO NRs/Si, H:ZnO NRs-350/Si and ZIF-8@H:ZnO NRs/Si.)

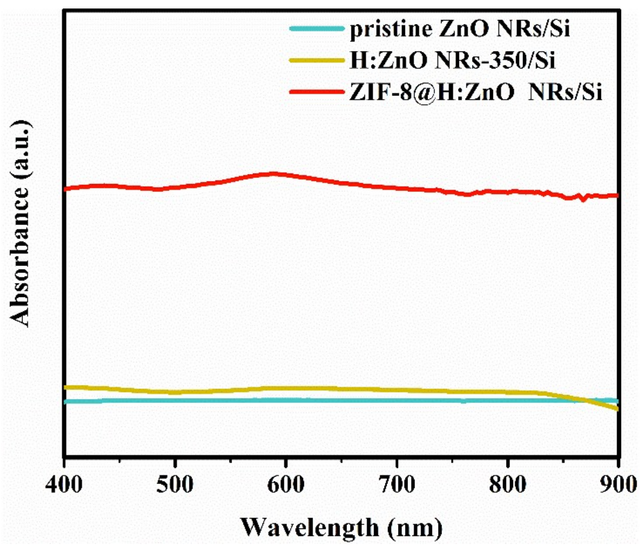

Figure S10. The absorption spectra of pristine ZnO NRs/Si, H:ZnO NRs-350/Si and ZIF-8@H:ZnO NRs/Si respectively.

Table S1. Performance comparison of our ZIF-8@H:ZnO NRs/Si heterojunction self-powered photodetector with previous reported ZnO-based self-powered devices.

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
H:VZnO nanoflakes/ PEDOT:PSS	p-n	365	2.65	5.25×10^{10}	23/26	1
ZnO/graphene/Cu_2O	p-g-n	365	21.2		6/6	2
Cl-ZnO nanorods /DMSO-PEDOT: PSS	p-n	365	0.80	1.12×10^{10}	30/32	3
ZnO/ZnS	n-n	340	56		40/40	4
ZnO homojunction nanofibers	p-n	360	1		3900/4700	5
ZnO nanorods /RGO	p-n	365			100/200	6
ZnO/Spiro-MeOTAD	p-n	365	0.8	4.2×10^{9}	160/200	7
Ga:ZnO nanorods /p-GaN	p-n	365	230	2.32×10^{12}		8
Pt/Al_2O_3/ZnO	MIS	Xe lamp	1.78×10^{-3}	7.99×10^{7}	100/100	9
CuSCN/ZnO nanorods	p-n	365	22.5		3200/3840	10
Au/MoO_3/Perovskite /ZnO nanorods	heterojunction	500	2.43×10^{4}	3.56×10^{14}	700/600	11
Pd/ZnO/Al	MSM	370	230		10/10	12
Graphene/ZnO nanowires/graphene	MSM	365	0.54			13

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
ZnO nanorods /p-Si	p-n	395			25/22	14
Au/ZnO/Au	MSM	365	30		0.71 μs/4 μs	15
Graphene/ZnO:Al nanorods	Schottky	380	39		0.037/0.33	16
P3HT/ZnO nanowires	p-n	365	0.125	3.7×10^{7}	100/100	17
ZnO/NiO	p-n	372	0.493		1.38 μs	18
Cl:ZnO nanorods /PEDOT:PSS	p-n	365	2.3354	1.5414×10^{10}	28/23	19
ZnO/Ga_2O_3	n-n	251	9.7	6.29×10^{12}	0.1/0.9	20
ZnO/CNTs	Schottky	325	2.75×10^{4}		0.48/0.65	21
ZnO nanowires/ CuSCN	p-n	370	20			22
ZnO nanowires /Si	p-n	1064	220		15 μs/21 μs	23
Pt/ZnO	Schottky	365	1.82		81/95	24
ZnO/Cu_2O	p-n		7.7×10^{-3}		90/90	25
Graphene/ZnO /n-Si	g-n-n	488	500		0.28/0.54	26
ZnO/p-Si	p-n	450			130	27

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
β-Ga_2O_3/Ga:ZnO	n-n	254	0.763		179/272	[28]
ZnO/Spiro-MeOTAD	p-n	390	17		0.2/0.95	[29]
		470	6.5		4/10	
Au/ZnO	Schottky	325			10/10	[30]
ZnO/MgO/GaN	p-i-n	350	320	8.0×10^{12}		[31]
Perovskite/ZnO nanoparticles	heterojunction	405	11.5		409/17.92	[32]
Au/α-Ga_2O_3/ZnO	Schottky+ n-n	230	3.42	9.66×10^{12}		[33]
ZnO nanowires/ PEDOT:PSS	p-n	325	3.5	7.5×10^{9}	5.8/7.3	[34]
ZnO nanowires /PVK	p-n	325	9.96		1500/6000	[35]
Perovskite/ZnO	heterojunction	325	26.7	4.0×10^{10}	0.053/0.063	[36]
ZnO/Se	p-n	370	2.56		0.69/13.5	[37]
ZnO/$CuCrO_2$ nanowires	p-n	395	5.87		0.032/0.035	[38]
ZIF-8@H:ZnO NRs/Si	p-n	365	209.6	6.354×10^{13}	0.252/0.607	This work
		650	536	1.625×10^{14}		

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
ZIF-8@H:ZnO NRs/Si	p-n	900	7.07×10^4	2.142×10^{16}	0.252/0.607	This work

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Table S2. Performance comparison of our ZIF-8@H:ZnO NRs/Si heterojunction self-powered photodetector with other previous reported self-powered devices.

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
Graphene/Si	Schottky	532	510		0.13/0.135	1
Au/InSe	Schottky	365	369			2
		685	244		23/25	
Au/PS-$MAPbI_3$	Schottky	710	610	1.5×10^{13}	13/14	3
Diamond/ β-Ga_2O_3	p-n	244	0.2	6.9×10^{9}		4
NiO/TiO_2 NRs	p-n	380	1.34	5.92×10^{11}	100/100	5
NiO/TiO_2 NRs /TiO_x			5.66	2.5×10^{12}		
Ag/Graphene /GaAs	van der Waals heterojunction	405	210	2.98×10^{13}		6
$PtSe_2$/Perovskite	Schottky	808	117.7	2.91×10^{12}	78/60 ns	7
CdS NRs/RGO	Schottky	530	0.58	7.2×10^{11}	1.3/1.7	8
$MoTe_2$/MoS_2	Van der Waals heterojunction	637	46		0.06	9
GaSe/WS_2	p-n	350	90		37/43 µs	10
Au/Perovskite	Schottky	650			45/91 ns	11

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
TiO_2/graphene /Perovskite	heterojunction	530	0.375	4.5×10^{11}	5/5	[12]
Graphene/Si	Schottky	750	400	5.4×10^{12}	6.7/8.6	[13]
MoS_2/GaAs	heterojunction	635	419	1.9×10^{14}	0.017/0.031	[14]
RGO/Si	p-n	600	1520		2/3.7	[15]
GaN/SiO_2 /MoS_2	heterojunction	633			400/350	[16]
RGO-MoS_2/ pyramid Si	heterojunction	808	2.18×10^4	3.8×10^{15}	2.8/46.6 µs	[17]
MoS_2/Perovskite	heterojunction	white light	60		2149/899	[18]
GaN microwires array/Si	p-n	325	131	3.4×10^{12}	2/2	[19]
		700	310	9.5×10^{12}	8/8	
		825	474	3.4×10^{12}	9/8	
$CsPbBr_3$-Cs4$PbBr_6$	heterojunction	254	49.4	1.2×10^{12}	7.8/33.6 µs	[20]
Bi_2Se_3/Si	heterojunction	808	2.6×10^3	4.39×10^{12}	2.5/5.5 µs	[21]
TiN:PPA	hybrid	570	570	1.92×10^{11}	9.23/18.12	[22]
MoO_{3-x}/Si	n-n	900		6.29×10^{12}	1/51.4 µs	[23]

Photodetector	Type	λ (nm)	Responsivity (mA/W)	Detectivity (Jones)	T_r/T_d (ms)	Ref.
γ-In_2Se_3/Si	p-n	820	800		0.175/0.226	24
CuO/Si nanowires	p-n	405	0.389	3.00×10^9	60/80 μs	25
		532	0.105	1.00×10^9		
		1064	0.064	7.60×10^9		
MoS_2/Si	p-n	808	300	10^{13}	3/40 μs	26
C Quantum dots/Si nanowires	heterojunction	600	353	3.79×10^9	20/40 μs	27
Se/TiO_2 nanotubes	p-n	620	100	6.2×10^{12}	1.4/7.8	28
SnTe/Si	heterojunction	808	128	8.4×10^{12}	8/390 μs	29
ZIF-8@H:ZnO nanorods/Si	p-n	365	209.6	6.354×10^{13}	0.252/0.607	This work
		650	536	1.625×10^{14}		
		900	7.07×10^4	2.142×10^{16}		

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