Electronic Supplementary Information

Optically coupled engineered upconversion nanoparticles and graphene for a high responsivity broadband photodetector

Mukesh Kumar Thakur, [1] Akash Gupta, [1] Muhammad Yusuf Fakhri, [2] Ruei San Chen, [2] Chien Ting Wu,[3] Kung Hsuan Lin,[4] and Surojit Chattopadhyay* [1]

[1]Institute of Biophotonics, National Yang Ming University, 155, sec-2 Li Nong Street, Taipei 112, Taiwan.

[2]Graduate Institute of Electro-Optical Engineering, National Taiwan University of Science and Technology, Section 4, Keelung Rd, Daan District, Taipei 106, Taiwan.

[3]Nano Device Materials Characterization Division, National Nano Device Laboratories, Hsinchu-300, Taiwan.

[4]Institute of Physics, Academia Sinica, No. 128, Sec. 2, Academia Rd., Nangang Dist., Taipei 11529, Taiwan.

*Corresponding author E-mail: sur@ym.edu.tw

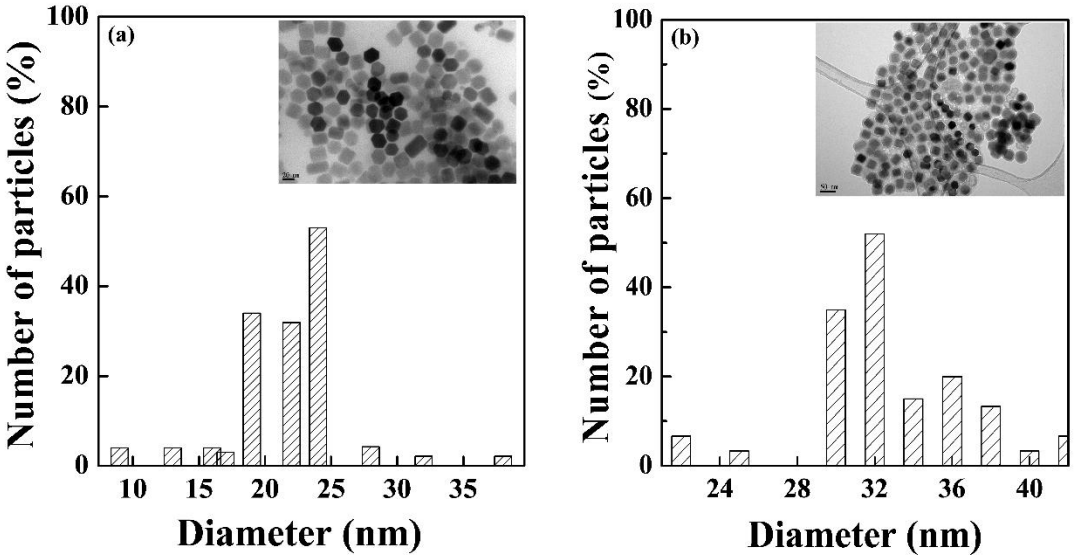

Fig.S1. Histograms showing the size distribution of the (a) core, and (b) core-shell UCNPs obtained from several TEM images. Insets in (a), and (b) show representative low resolution TEM images for the core, and coreshell UCNPs.

The histograms show the size distribution of the core, and core-shell UCNPs. There are very few UCNPS which are either too small or too large and constitute less than 10% of the UCNPs accounted for. Majority of the UCNPs show a size distribution near 20-25 nm for the core, and 30-36 nm for the core-shell UCNPs. So the size distribution for the core, and core-shell UCNPs are 22±3, and 33±3 nm, respectively.

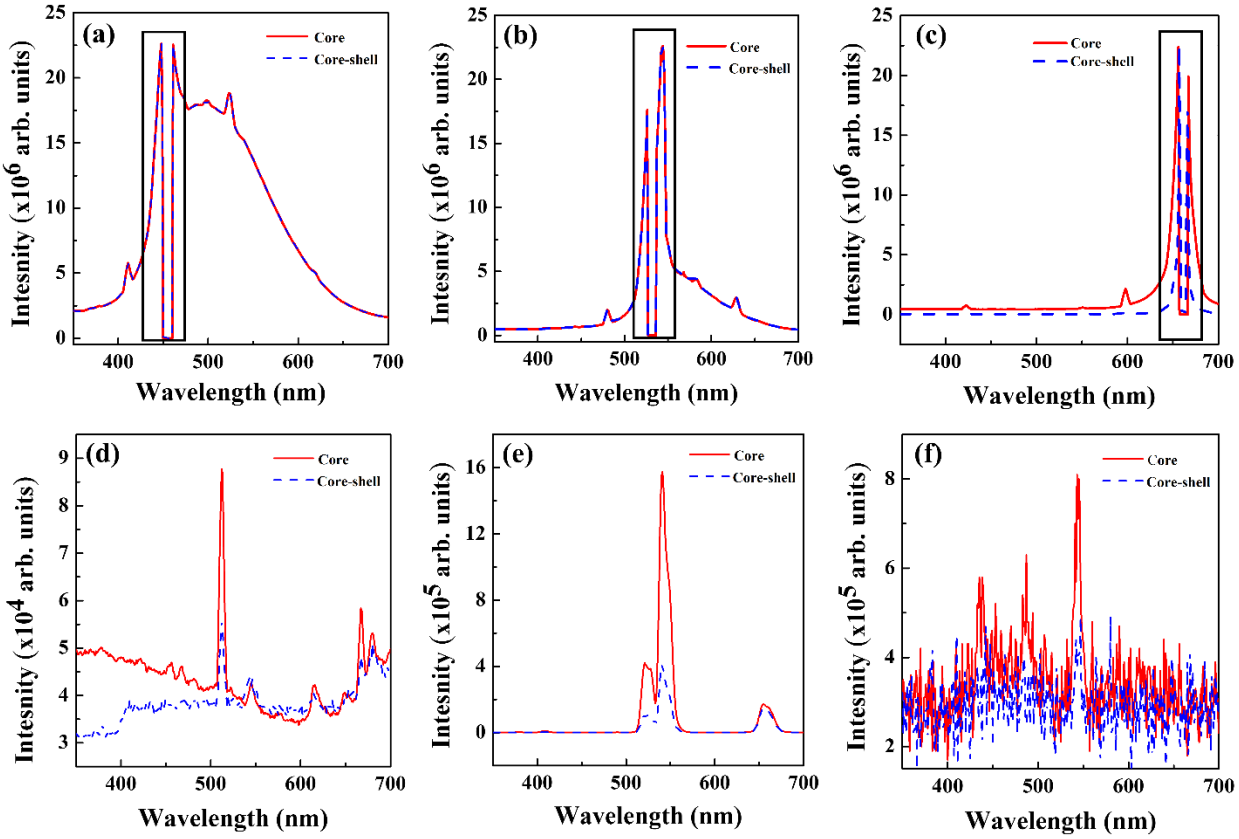

Fig.S2. Photolumniscence spectra of core (red solid line) and core-shell (blue dashed line) UCNPs for (a) 405, (b) 532, (c) 655, (d) 808, (e) 980, and (f) 1064 nm excitation. The signals in the black box (a-c) indicates the strong laser exciation. The dip in those signals (a-c) indicates detector saturation. The power for 405, 532, 655, and 1064 nm excitation is 100 mwatt. 5 Watt of the 808, and 1 W of 980 nm laser was used in (d), and (e), respectively.

Among all the fluorescence spectra (Fig. S2a-f), the one under 980 nm excitation shows strongest emission (Fig. S2e). Under 808 nm excitation, there is a strong emission at 512 nm for both core, and core-shell UCNPs (Fig. S2d) although much weaker than the 520/540 nm peak under 980 nm excitation. This may be due to weak non-resonant 808 nm absorption in the Yb.[1] Weak 540, and 650 nm emissions could also be observed under 808 nm excitation (Fig. S2d). Researchers have observed a weak 512 nm emission even under 980 nm excitation previously,[2] but did not comment on its source transition. From the electronic energy level perspective, the 512 nm emission may

come from a state higher than the $2H_{7/2}$ state responsible for the 520 nm emission. It may be from the $4F_{7/2}$ that generally provides for the non-radiative transitions (see Fig. S5).

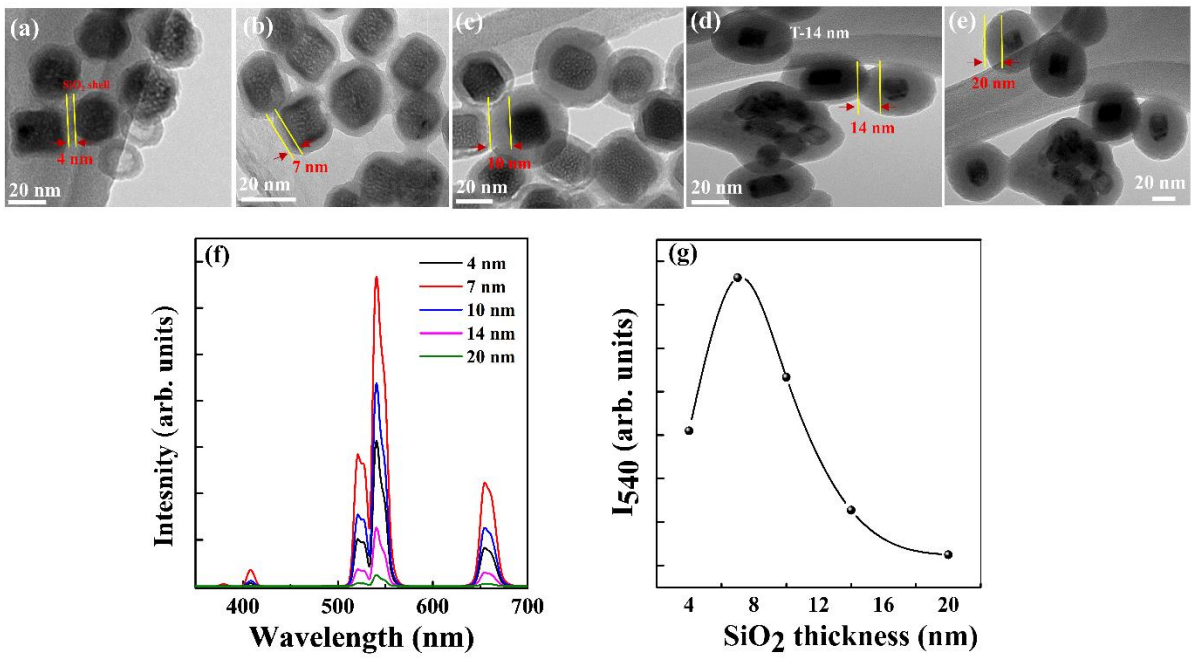

Fig.S3. TEM images of core shell UCNPs having different SiO_2 thicknesses of (a) 4, (b) 7, (c) 10, (d) 14 , and (f) 20 nm. The yellow lines mark the thickness of the SiO_2 layer. (f) Fluorescence spectra of core-shell UCNPs on graphene having different SiO_2 thickness under 980 nm (7.96 Wcm^{-2} power) excitation. (g) The variation of the intensity of the green emission band (I_{540}) as a function of the SiO_2 shell thickness of core-shell UCNPs on graphene. The line joining the data points is a guide to the eye only.

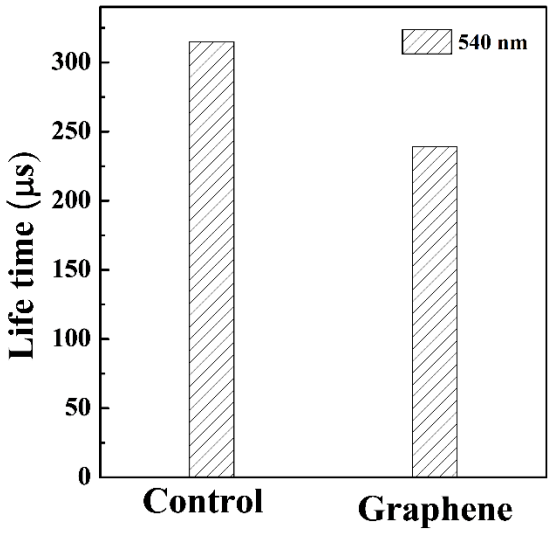

Fig.S4. Fluorescence life time of the green emission in powder UCNP@SiO_2 without (Control), and with optimized graphene.

Lifetime measurements were done in the frequency domain[3] on the substrates. These surfaces were dispersed with core-shell UCNPs, with and without graphene, and lifetimes measured for the major 540 nm emission peak. The fluorescence life time (τ), in the frequency domain, was calculated by the general equation $\boldsymbol{\tau = \frac{tan\Phi}{\omega}}$, where ω=2πf, f being the chopping frequency, and φ is the phase difference between excitation, and emitted light. First, the phase difference $\varphi = \varphi_2 - \varphi_1$ is measured, where φ_2 and φ_1 are phase of emitted, and excitation (980 nm) light, respectively. We have measured the emission life time with f= 425 Hz chopping frequency. The observed fluorescence lifetime is clearly decreased for the sample in presence of graphene. Such decrease in fluorscence lifetime has been observed in UCNPs in presence of metallic plasmons that enhanced its fluorescence.[4]

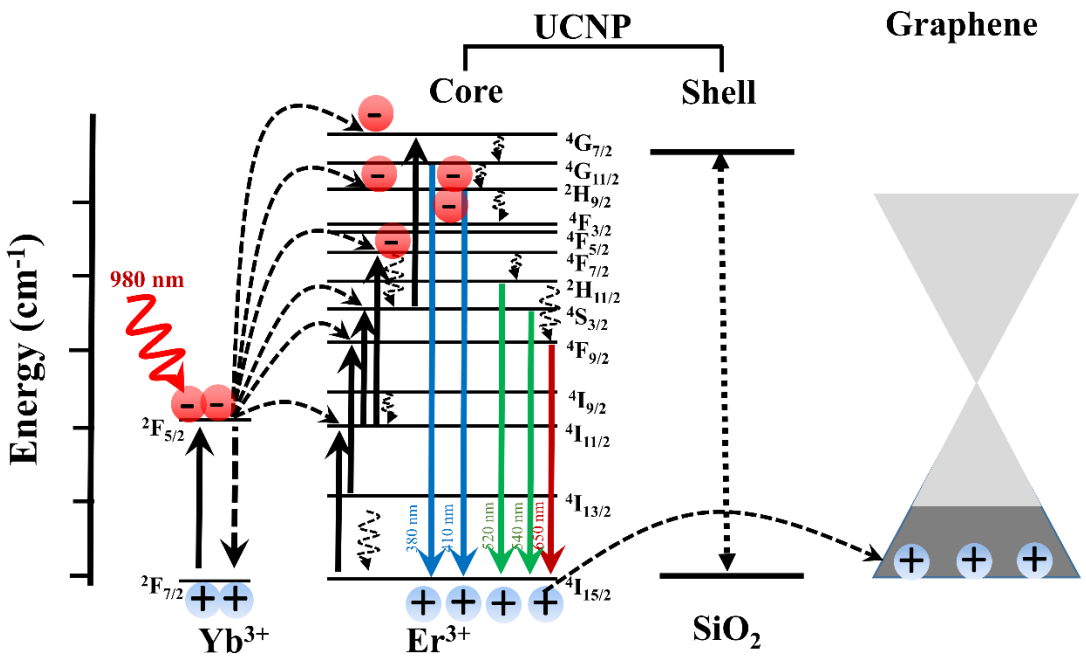

Fig.S5. The schematic energy band diagram, and charge transfer in core-shell UCNP-Graphene based photodetctor. SiO_2 is the shell used in this work. + and – indicate holes, and electrons, respectively. Wavy arrows indicate thermalization. Straight arrows indicate radiative transitions giving rise to different fluorescence lines in UCNP (Erbium doped). Curved arrows indicate charge excitation/transfer in UCNP, and graphene. The schematic is not drawn to scale.

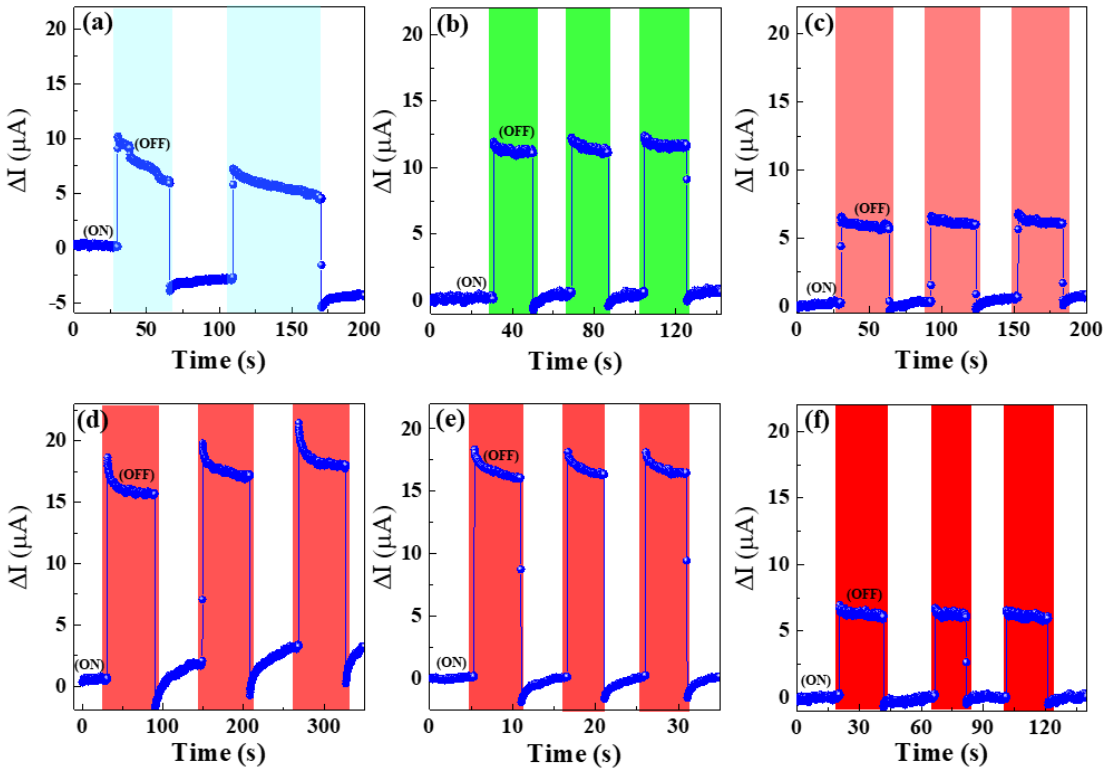

Fig. S6. The photo-response of core UCNP-graphene device under the illumination of (a) 405, (b) 532, (c) 655, (d) 808, (e) 980, and (f) 1064 nm, at a laser power density ~ 31.84 μWcm^{-2} and V_{DS} = 1 Volt.

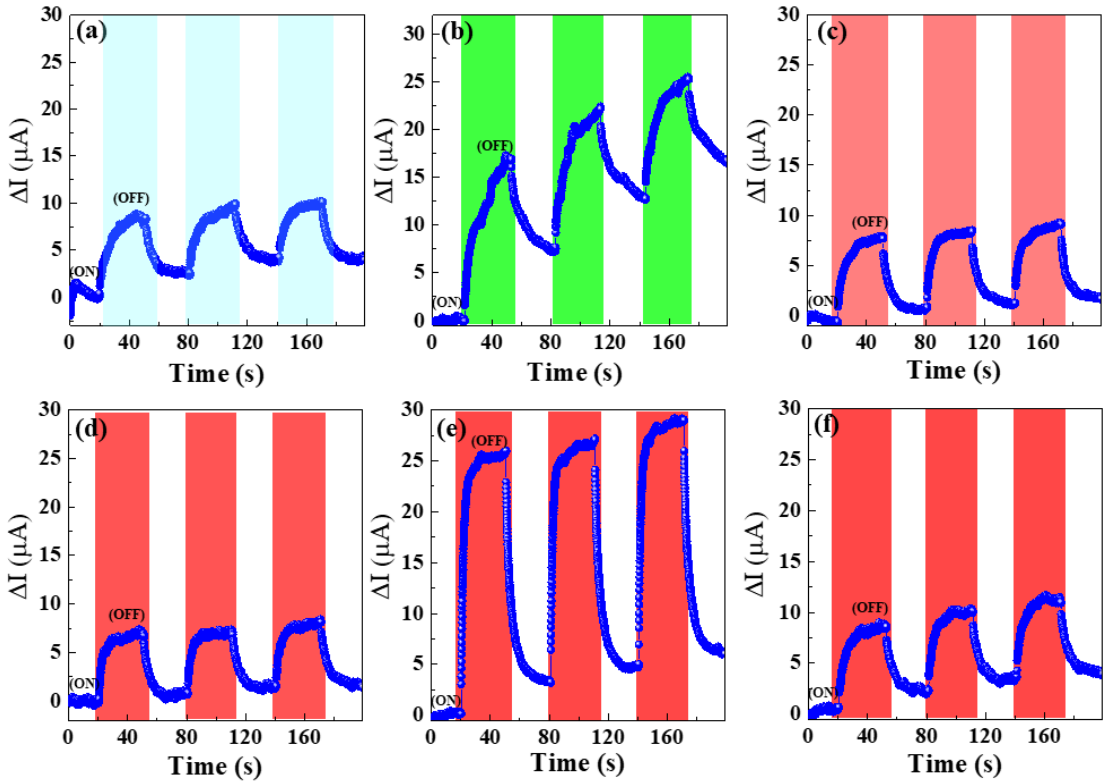

Fig. S7. The photo-response of core-shell UCNP-graphene device under the illumination of (a) 405, (b) 532, (c) 655, (d) 808, (e) 980, and (f) 1064 nm, at a laser power density ~ 31.84 μWcm^{-2} and V_{DS} = 1 Volt.

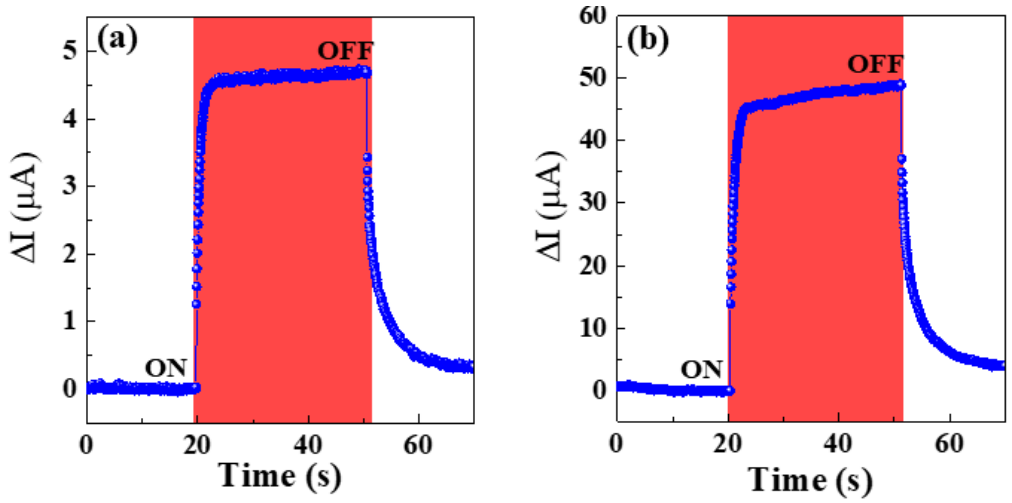

Fig. S8. Dynamic photoresponse of the core-shell UCNP-graphene hybrid PD device showing photocurrent saturation at 23.88 $mWcm^{-2}$ of 980 nm laser with V_{DS} of (a) 0.1, and (b) 1.0 Volt.

Table S1. Photodetector device parameters for both core, and core-shell UCNP based hybrid device under different illumination wavelength

Wavelength (nm)	Responsivity (@V_{DS}= 1V, 31.84 μWcm^{-2}) (A/W)		Normalized gain (@V_{DS}= 1V, 31.84 μWcm^{-2}) (10^{-4} m^2 V^{-1})		Detectivity (@V_{DS}= 1V, 31.84 μWcm^{-2}) (x10^{12} Jones)	
	Core	Core-Shell	Core	Core-Shell	Core	Core-Shell
405	2125	1993	0.06	0.19	0.52	0.51
532	2875	6743	0.21	0.49	0.40	1.64
655	2717	4386	0.16	0.26	0.87	1.27
808	3617	1196	0.16	0.07	0.33	0.52
980	**15189**	**26914**	**0.60**	**1.07**	**5.30**	**7.7**
1064	2607.94	1744	0.09	0.06	0.57	0.96

The highlighted part in the table indicates the highest Responsivity, Normalized gain, and Detectivity for the PD device.

Table S2. Comparison of device performances of UCNPs based photodetectors.

Material	**Wavelength (nm)**	**V_{DS} (V)**	**Power**	**R (A/W)**	**Γ_n (m^2V^{-1})**	**Ref**
$CuInS_2$/ZnS/$NaYF_4$:Yb,Er/ $NaYF_4$	980	1	25 mW	--	--	5
GO-Au Film $NaYF_4$:Yb,Tm@$NaYF_4$ UCNPs	980	0.01	8 W/cm^2	--	--	4
$NaYF_4$:Yb/Er@$NaYF_4$:Nd/Yb)/MoS_2	980	1	0.64 W/cm^2	10.5 x 10^{-3}	--	6
$MAPbI_3$-UCNPs	980	2	60 mW/cm^2	0.27	--	7
$NaYF_4$:Yb:Er:Nd@$NaYF_4$: Nd)/ graphene	808	1	0.1μW	190	--	8
$NaYF_4$:Yb/Er@SiO_2/graphene	**980**	**1**	**31.84 μW/cm^2**	**26914**	**10^{-4}**	**This work**

Note: R: Responsivity; Γ_n: Normalized gain.

References (for ESI only):

1. Y. Zhnag, J. Wang, B. Wang, J. Shao, J. Deng, C. Cong, L. Hu, P. Tian, R. Liu, , S. L. Zhang, and Z. J. Qiu, *Adv. Opt. Mat*., 2018, **6**,1800660.

2. G. Chen, H. Qiu, P. N. Prasad, and X. Chen, *Chemical Review, 2014*, **114**, 5161–5214.

3. G. I. Redford, and R. M. Clegg, *J. Fluoresc*., 2005, **15**, 805.

4. W. Niu, H. Chen, R. Chen, J. Huang, A. Palaniappan, H. Sun, B. G. Liedberg and A. I. Y. Tok, *Small*, 2014, **10**, 3637-3643.

5. A. R. Hong, J. Kim, S. Y Kim, S. I. Kim, K. Lee and H. S Jang, *Optics Letters,* 2015, **40**, 4959-4962.

6. N. Zhou, B. Xu, L. Gan, J. Zhang, J. Han, and T. Zhai, *J. Mater. Chem. C.*, 2017, **5**, 1591-1595

7. J. Li, Y. Shen, Y. Liu, F. Shi, X. Ren, T. Niu, K. Zhao and S. Liu, *ACS Appl. Mater. Interfaces.*, 2017, **9**, 19176-19183

8. M. Kataria, K. Yadav, G. Haider, Y. M. Liao, Y. R. Liou, S .Y Cai, H. I. Lin,Y. H. Chen, C. R. Paul Inbaraj, K. P. Bera, H. M. Lee, Y. T Chen, W. H. Wang and Y. F. Chen, *ACS Photonics,* 2018, **5**, 2336-2347.