## Electronic Supplementary Information

## Plasmon-Mediated Wavelength-Selective Enhanced Photoresponse in Polymer Photodetectors

Huan Wang,<sup>a</sup> Ju Won Lim,<sup>a</sup> Filipe Marques Mota,<sup>a</sup> Yu Jin Jang,<sup>a</sup> Minji Yoon,<sup>a</sup> Heejun Kim,<sup>a</sup> Wei Hu,<sup>b</sup> Yong-Young Noh,<sup>c</sup> and Dong Ha Kim<sup>\*,a</sup>

<sup>a</sup> Department of Chemistry and Nano Science, Division of Molecular and Life Sciences,
College of Natural Sciences, Ewha Womans University, 52, Ewhayeodae-gil, Seodaemungu, Seoul 120-750, Korea

<sup>b</sup> Key Laboratory for Micro-Nano Physics and Technology of Hunan Province, and School of Physics and Electronics, Hunan University, 2 Lushan S. Rd, Yuelu, Changsha, Hunan 410082, P. R. China

<sup>c</sup> Department of Energy and Materials Engineering, Dongguk University, 26 Pil-dong, 3-ga, Jung-gu, Seoul 100-715, Korea



**Figure S1.** Photocurrent of photodiodes with AgNPs (a), AuNPs (b) and AuNRs (c) of different dipping time under blue, green and red light illumination (15 mW/cm<sup>2</sup>), respectively. The dipping time of 30 min for AgNPs, 30 min for AuNPs and 60 min for AuNRs are the optimized condition in the devices, respectively, which can obtain the maximum photocurrent.



**Figure S2.** AFM images and corresponding absorbance of AgNPs (a), AuNPs (b) and AuNRs (c) adhered on the substrates with different dipping time. With increasing the amounts of plasmonic nanoparticles, the stronger SPR band will be red-shift and wider.



**Figure S3.** (a) Optical photographs of bare, AgNPs, AuNPs and AuNRs covered with ZnO layer, respectively; (b, c) AFM images and absorption spectra of P3HT:PCBM films (pristine as reference) including AgNPs, AuNPs and AuNRs structures, respectively, with ZnO layer as the spacer (The scale bar is 500 nm); (d) Cross-section analysis of P3HT:PCBM film of ~270 nm thickness.



**Figure S4.** Height contrast AFM images and cross-sectional analyses of  $\sim$ 15 nm AgNPs arrays on the substrate (a) and  $\sim$ 25 nm ZnO layer coating on the AgNPs arrays (b). The actual distance between AgNPs and the active layer is  $\sim$ 18 nm.



**Figure S5.** Height contrast AFM images and cross-sectional analyses of  $\sim$ 20 nm AuNPs arrays on the substrate (a) and  $\sim$ 25 nm ZnO layer coating on the AuNPs arrays (b). The actual distance between AuNPs and the active layer is  $\sim$ 20 nm.



**Figure S6.** Height contrast AFM images and cross-sectional analyses of  $\sim$ 40/80 nm AuNRs arrays on the substrate (a) and  $\sim$ 25 nm ZnO layer coating on the AuNRs arrays (b). The actual distance between AuNRs and the active layer is  $\sim$ 15 nm.



Figure S7. Phase contrast AFM images of  $\sim$ 40/80 nm AuNRs arrays on the substrate (a) and  $\sim$ 25 nm ZnO layer coating on the AuNRs arrays (b).



**Figure S8.** Phase contrast AFM images of P3HT:PCBM films (pristine as reference) including AgNPs, AuNPs and AuNRs nanostructures, respectively, with ZnO layer as the spacer.



**Figure S9.** Current density–voltage characteristics of photodiodes without (pristine as reference)/with AgNPs (a), AuNPs (b) and AuNRs (c) in dark and under blue (450 nm), green (525 nm) and red (620 nm) light illumination (15 mW/cm<sup>2</sup>), respectively.



**Figure S10.** SEM images and absorbance of AgNPs (~15 and 70 nm), AuNPs (~20 and 55 nm) and AuNRs (~40/80 and 30/90 nm) deposited on the substrates. The diameter and aspect ratio of plasmonic nanostructures dictate their respective SPR bands.



**Figure S11.** (a, c, e) Photocurrent of photodiodes with AgNPs, AuNPs and AuNRs of different size under blue (450 nm), green (525 nm) and red (620 nm) light illumination (15 mW/cm<sup>2</sup>), respectively; (b ,d, f) Dark current of the above corresponding photodiodes.



**Figure S12.** Calculated responsivities (a) and detectivities (b) of photodiodes with AgNPs, AuNPs and AuNRs of different size for blue, green and red light detection, respectively. Photocurrent and dark current values were taken at the voltage of -0.5 V, and light intensity is 15 mW/cm<sup>2</sup>.



Figure S13. (a, c) ON-OFF photoresponse of photodiodes without (pristine as

reference)/with AgNPs, AuNPs and AuNRs under green (525 nm) and blue (450 nm) light illumination (15 mW/cm<sup>2</sup>), respectively; (b, d) Normalized current curves of corresponding photodiodes. All devices were measured in air.



**Figure S14.** Device stability: Evolution of normalized photocurrent as a function of time for photodiodes without (pristine as reference)/with AgNPs, AuNPs and AuNRs under green (a) and blue (b) light illumination (15 mW/cm<sup>2</sup>), respectively. The photodiodes were stored in air over ten days and the recorded photocurrent values are summarized in Table S1. All devices were measured in air.

**Table S1.** Device stability: photocurrent values ( $J_{ph}$ , mA/cm<sup>2</sup>@-0.5 V) of pristine and AgNPs, AuNPs and AuNRs-mediated photodiodes under blue (450 nm), green (525 nm) and red (620 nm) light illumination (15 mW/cm<sup>2</sup>) with varying time. All devices were stored and measured during ten days in air.

Time (days)		0	1	2	3	4	5	6	7	10
Blue (450nm)	pristine	2.12	2.05	1.97	1.88	1.76	1.67	1.56	1.42	1.24
	w. AgNP	3.09	3.02	2.93	2.82	2.69	2.55	2.43	2.31	2.10
	w. AuNP	2.73	2.64	2.53	2.45	2.32	2.19	2.05	1.89	1.70
	w. AuNR	2.36	2.28	2.17	2.08	1.96	1.83	1.70	1.55	1.38
Green (525nm)	pristine	2.60	2.51	2.43	2.31	2.18	2.03	1.90	1.78	1.56
	w. AgNP	2.77	2.67	2.58	2.45	2.37	2.25	2.12	2.00	1.81
	w. AuNP	3.95	3.83	3.73	3.65	3.53	3.40	3.27	3.11	2.87
	w. AuNR	3.22	3.13	2.99	2.88	2.78	2.65	2.51	2.37	2.05
Red (620nm)	pristine	2.19	2.11	2.02	1.91	1.78	1.70	1.62	1.55	1.31
	w. AgNP	2.25	2.18	2.09	2.01	1.89	1.77	1.71	1.63	1.35
	w. AuNP	2.85	2.76	2.63	2.51	2.37	2.29	2.15	2.06	1.78
	w. AuNR	3.72	3.66	3.51	3.42	3.30	3.18	3.05	2.89	2.65



**Figure S15.** Absorption (a) and emission spectra under the excitation wavelength  $\lambda_{ex} = 440$  nm (b) and  $\lambda_{ex} = 590$  nm (c) of P3HT films (pristine as reference) including AgNPs, AuNPs and AuNRs, respectively, with ZnO layer as the spacer.



Figure S16. J-V curves of pristine and plasmon-mediated devices working in photovoltaic mode.

Devices	$V_{\rm oc}$ (V)	$J_{\rm sc}$ (mA/cm <sup>2</sup> )	FF (%)	PCE (%)
pristine	0.618	8.59	60.53	3.21
w. AgNP	0.592	9.24	65.59	3.59
w. AuNP	0.593	10.06	64.92	3.87
w. AuNR	0.598	9.75	67.25	3.92

Table S2. Summary of solar cell parameters of pristine and plasmon-mediated devices.