Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Information for

Improvement of polypyrrole nanowire device by plasmonic space charge generation: high photocurrent and wide spectral response by Ag nanoparticle decoration

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I. SEM image of crude PPy NWs and TEM image of PPy NW

Figure S1(a) shows a SEM image of bundles of the negatively charged PPy NWs just after removal of AAO template. It shows that length of the PPy NWs is ~ 40 μm. Figure S1(b) shows a TEM image of an individual PPy NW. As shown in the inset (top-left) of Figure S1(b), the diffraction image of the PPy NW displays concentric ring pattern. Thus, it is considered that the PPy NW is non-single crystalline.

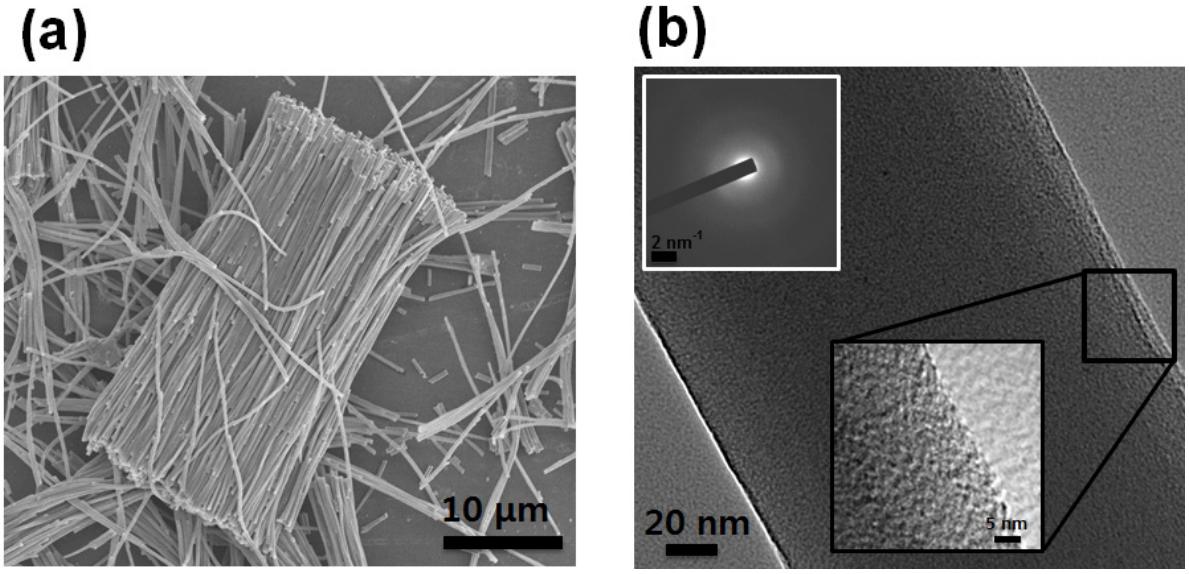

Figure S1. (a) A SEM image of crude PPy NWs. (b) A TEM image of PPy NW. Insets: diffraction image (top-left) and zoomed image (bottom).

II. Fabrication of PPy NW and PPy_{AgNPs} NW devices

PPy NWs and PPy_{AgNPs} NWs were dispersed on a microelectrode-chip as shown in Figure S2(a) and S2(c), respectively. The microelectrode-chips have been fabricated using photolithography. The geometry of the microelectrode is 18 channels, 2 μm of electrode width, and 3 μm of gap in the center area. The electrodes were thermally deposited with 45 nm-thick Au film with 7 nm of Ti buffer layer on a SiO_2 substrate. It has been reported that PPy NWs fabricated with $LiClO_4$ counter ion have high conductivity and good Ohmic contact on Au electrodes.[1] No treatment for having Ohmic contact was carried out in the PPy NW and PPy_{AgNPs} NW devices; nevertheless, the devices show Ohmic behavior in the low voltage region as shown in Figure S5. SEM images of typical PPy NW and PPy_{AgNPs} NW devices are displayed in Figures S2(b) and S2(d), respectively. As the diameter of the NWs in the devices are not identical, current density (instead of current) is considered in characterization in the manuscript. Because size-dependent transport properties in PPy NWs are not meaningful in the case of NWs with 300–400 nm diameter,[2] effects of different diameters of the PPy NW and PPy_{AgNPs} NW devices on characterization is neglected. To minimize error due to geometry of devices, NW devices with similar diameters and lengths between the electrodes were chosen.

1.Jang, J.-W.; Sanedrin, R. G.; Senesi, A. J.; Zheng, Z.; Chen, X.; Hwang, S.; Huang, L.; Mirkin, C. A. *Small* **2009,** 5, (16), 1850-1853.

2.Duchet, J.; Legras, R.; Demoustier-Champagne, S. *Synth. Met.* **1998,** 98, (2), 113-122.

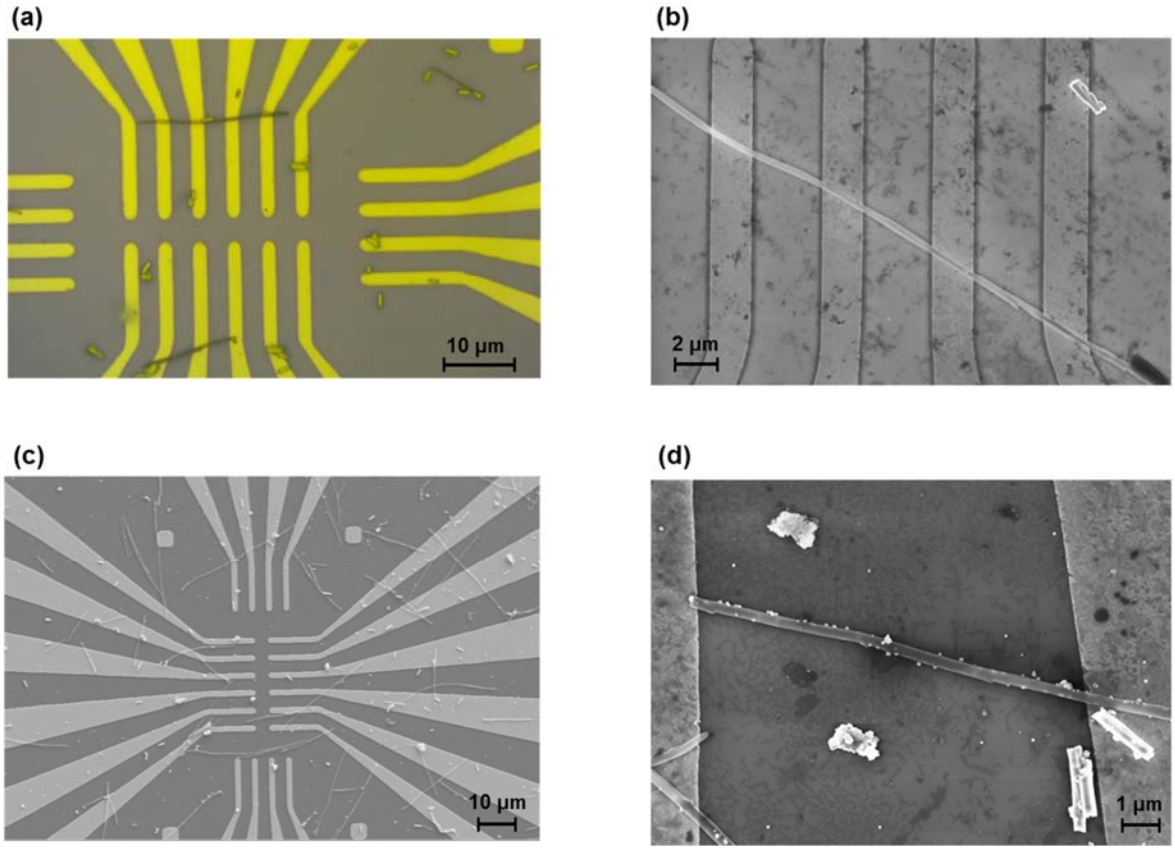

Figure S2. (a) Optical microscope image of PPy NWs on a microelectrode-chip. (b) SEM image of PPy NW device. (c) SEM image of PPy_{AgNPs} NWs on a microelectrode-chip. (d) SEM image of PPy_{AgNPs} NW device.

III. EDS analysis of PPy_{AgNPs} NW device

Energy-dispersive X-ray spectroscopy (EDS) has been carried out on the PPy_{AgNPs} NW device in order to confirm Ag NPs attachment. Figure S3 shows EDS spectrum obtained from PPy_{AgNPs} NW device as shown in the SEM image. Small wt% of Ag element (4.52%) indicates existence of Ag NPs in the area.

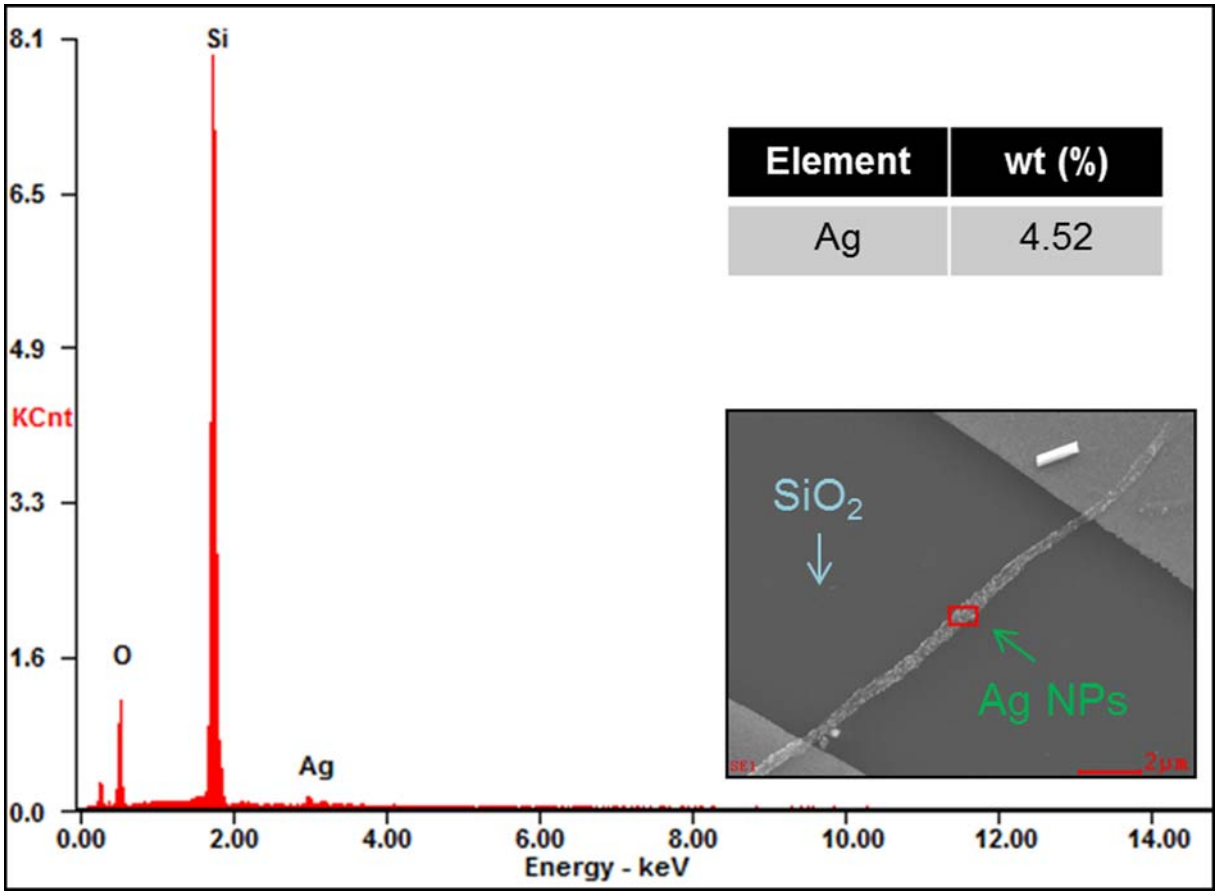

Figure S3. EDS spectrum of PPy_{AgNPs} NW device. Inset: SEM image of the PPy_{AgNPs} NW device.

IV. Control experiment of electrostatic Ag NPs decoration on PPy NWs

As a control experiment of electrostatic Ag NPs decoration on PPy NWs, the positively charged Ag NPs aqueous solution was blended into neutrally charged PPy NWs (without COOH group on the surface) aqueous solution. After stirring of the blended Ag NPs and PPy NWs solution, the PPy NWs were dispersed on a substrate to check Ag NPs decoration microscopically. Figure S4 shows that Ag NPs are not attached on PPy NW without COOH group on the surface. Therefore, it is known that electrostatic force mainly works on the Ag NPs decoration on the PPy NWs.

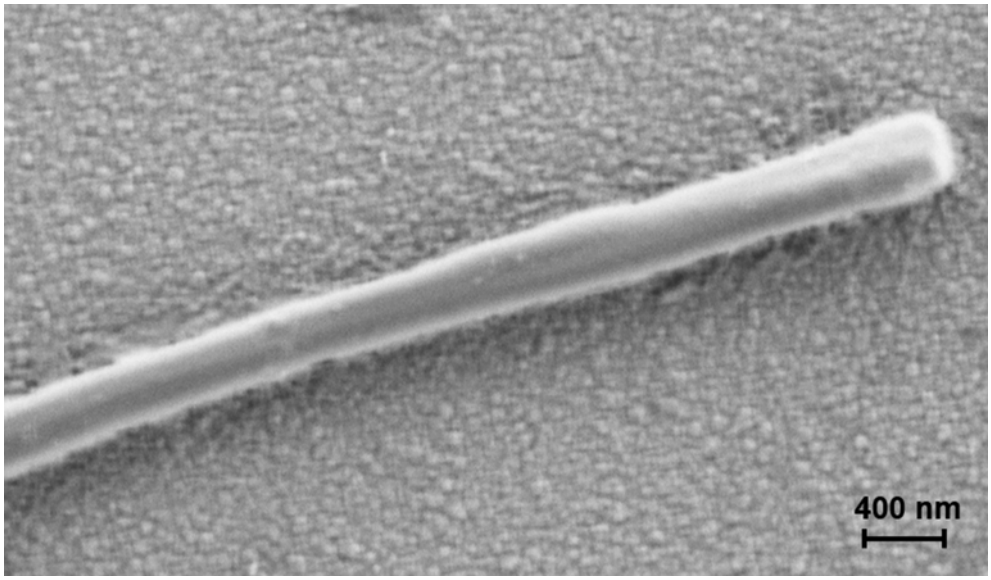

Figure S4. SEM image of PPy NW without superficial COOH group after blending with positively charged Ag NPs.

V. Ohmic behavior of PPy NW and PPy_{AgNPs} NW devices in low voltage region

The PPy NW and PPy_{AgNPs} NW devices represent Ohmic behavior in the voltage range lower than 0.1 V, as shown in Figure S5. The solid lines are fitted with power law ($J \propto V^m$). The exponent *m* is exactly 1 in both NW devices.

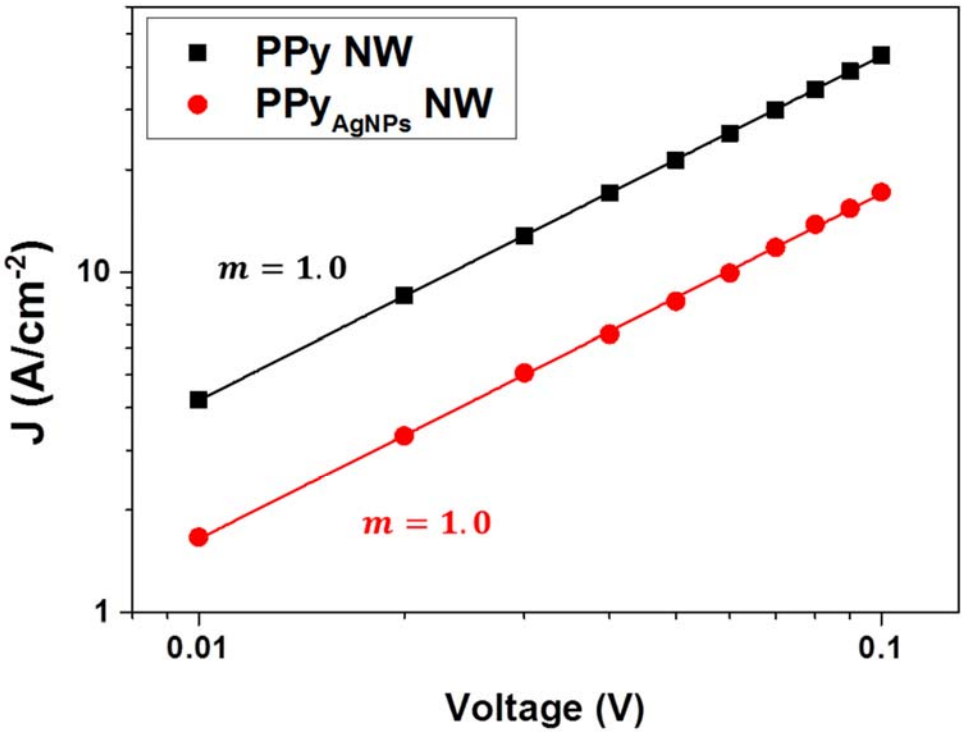

Figure S5. J–V curves of the PPy NW and PPy_{AgNPs} NW devices in low voltage region.

VI. Vector plots of *E*-field at interface between Ag NP and PPy NW

In Figure 5(a) and 5(b), the contour plots of *E*-field intensity (E^2) at the interface between Ag NP and PPy NW are displayed. To know direction of charge movement, vector plots of *E*-field are measured by FDTD simulation as shown in Figure S6. Under blue light illumination [Figure S6(a) and S(b)], *E*-field forms from the PPy NW to the Ag NP, while the opposite direction forms under red light illumination [Figure S6(d)]. This result matches well with the proposed mechanism shown in Figure 6. For red light illumination, holes moves from the interface to inside of the PPy NW [Figure 6(c)]. In case of blue light illumination, electrons are injected into PPy NW [Figure 6(d)].

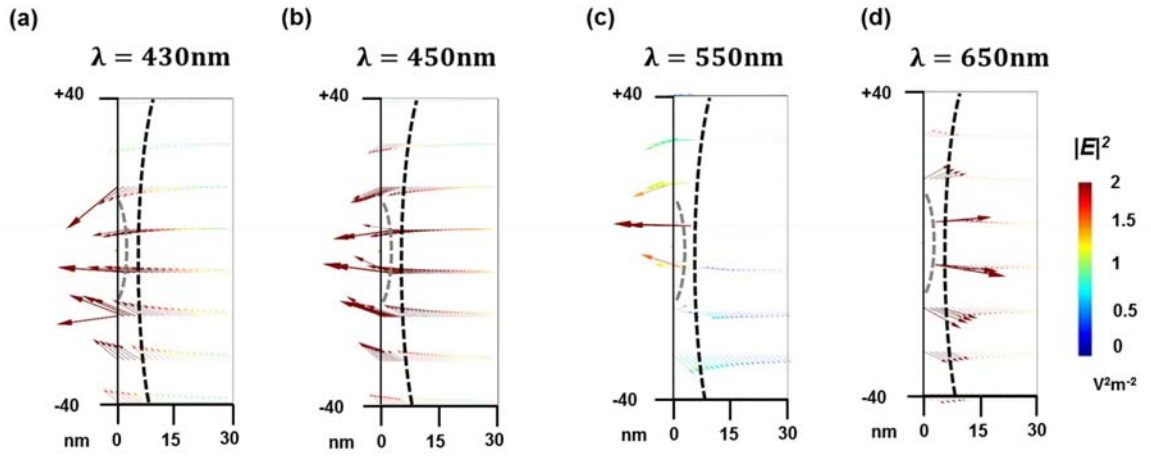

Figure S6. Vector plots of *E*-field at interface between Ag NP and PPy NW under certain wavelengths of light illumination: (a) 430 nm, (b) 450 nm, (c) 550nm, and (d) 650 nm. The gray dashed line represents boundary of Ag NP, and the black dashed line represents boundary of PPy NW.

VII. FDTD simulating absorption spectra

FDTD simulation on absorption spectra was also carried out. Figure S7 shows absorption spectra of single Ag NP and Ag NP dimer. The maximum absorption peak is red-shifted in the spectrum of Ag NP dimer. It is supposed that aggregation effect of Ag NPs is reflected on the absorption spectrum of Ag NPs shown in Figure 2(a). In addition, absorption spectra of PPy NW, single Ag NP attached PPy NW, and Ag NP dimer attached PPy NW are displayed in Figure S7(b). Absorption slightly increase by single Ag NP and Ag NP dimer attachment in the range of 400–550 nm, which corresponds well with absorption spectra of PPy NWs and PPy_{AgNPs} NWs shown in Figure 2(a).

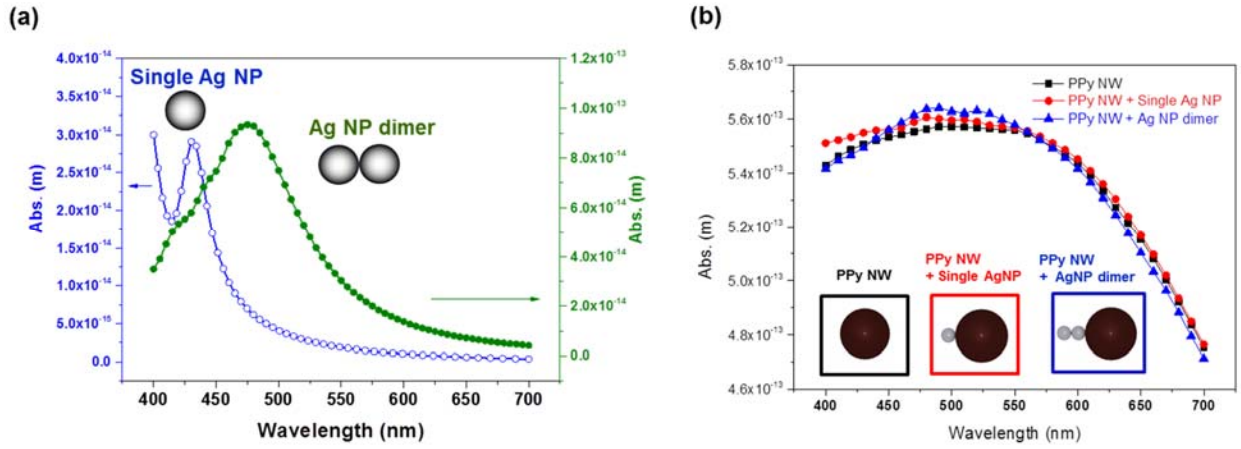

Figure S7. Absorption spectra obtained by FDTD simulation: (a) Single Ag NP and Ag NP dimer, (b) PPy NW, single Ag NP attached PPy NW, and Ag NP dimer attached PPy NW.