Supporting Information for

# Hot-electron-triggered catalytic oxidation reaction of plasmonic silver nanoparticles evidenced by surface potential mapping

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## I. Detail of V<sub>CPD</sub> measurements in PPy NWs

The bar graph of  $\Delta V_{CPD,450nm}$  for the oxidative and de-oxidative PPy NWs displayed in Figure 2(o) are averaged values from four (*Water*), four (*Heating*), three (*Vacuum* (1 day)), and three (*Vacuum* (2 days)) different PPy NW samples. Figure S1(a–i) displays topographic images (Figure S1(a)) and mapping images of V<sub>CPD</sub> obtained from another PPy NW on an Au substrate in dark (Figure S1(b–e)) and LSPR (Figure S1(f–i)) conditions for the environmental treatments in the order of water exposure (kept in water solution for 1 year), heating (vacuum oven at 80°C for 10 min), the first vacuum drying (in a vacuum desiccator for 1 day), and the second vacuum drying (for 2 days in total). The line profiles of the V<sub>CPD</sub> of the PPy NW obtained from the black dashed lines in Figure S1(b–e) and S1(f–i) are represented in Figures S1(j) and S1(k), respectively, which show similar V<sub>CPD</sub> changes dependent on the environmental treatments with the data shown in Figures 2(l) and 2(m). The  $\Delta V_{CPD,450nm}$  shown in Figure 2(o) have been obtained from subtracting the averaged V<sub>CPD</sub> values of the PPy NW under LSPR (V<sub>CPD</sub>(@450 nm)) condition in Figure S1(m)) from that of the PPy NW in dark (V<sub>CPD</sub>(@Dark) condition in Figure S1(l)).



**Figure S1**. (a) A topographic and (b–i)  $V_{CPD}$  mapping images of oxidative and de-oxidative PPy NW on an Au substrate in (b–e) dark and (f–i) LSPR conditions with environmental treatments carried out for samples in the manuscript (Figure 2). The black-dashed lines in (b–i) represent where the line profiles have been obtained. The scale bars in (a–i) are 300 nm. (j and k)  $V_{CPD}$  line profiles of the oxidative and de-oxidative PPy NW in (j) dark and (k) LSPR conditions with the environmental treatments. (1 and m) Bar graphs of (1)  $V_{CPD}$ (@Dark) and (m)  $V_{CPD}$ (@450nm) of the PPy NW with environmental treatments.

# II. V<sub>CPD</sub> of PPy NW with re-oxidative treatment

After the oxidative and de-oxidative treatments were carried out for PPy NWs on an Au substrate as represented in Figure S1 and Figure 2, the V<sub>CPD</sub> of the PPy NW with reoxidative treatment (exposure to water for 60 min) in dark condition was carried out to characterize the oxidation mechanism of PPy NW. Figure S2(a) shows another V<sub>CPD</sub> mapping image of PPy NW with de-oxidative treatment (the second vacuum drying for 1 day, making 2 days in total) in the dark condition, which is similar to Figures S1(e) and 2(e). Figure S2(b) displays a V<sub>CPD</sub> mapping image of the PPy NW with the re-oxidative treatment. The line profiles of the V<sub>CPD</sub> obtained from Figures S2(a) and S2(b) are as shown in Figure S2(c); the V<sub>CPD</sub> maximum of PPy NW with de-oxidative treatment is approximately 88 mV, and that of PPy NW decreases to approximately 54 mV with re-oxidative treatment. The decreasing  $V_{CPD}$  of PPy NW with the re-oxidative treatment means that the charge state at the surface of the PPy NW can be reversibly changed with the oxidation process (negatively changed by oxygen ions on the surface). Hence, we can conclude that the oxygen adsorbed at the surface of the PPy NW works as trap due to its reversibility. If the adsorbed oxygen decreases the anions at the surface of the PPy NW, the charge state at surface of the PPy NW will not be reversibly changed by the re-oxidation process because decreased anions are not fully recovered by the de-oxidation process.<sup>1</sup>



**Figure S2.** (a) A V<sub>CPD</sub> mapping image of PPy NW with de-oxidative treatment (the second vacuum drying for two days) in the dark condition. (b) A V<sub>CPD</sub> mapping image of PPy NW with the re-oxidative treatment (exposure to water for 60 min) in the dark condition. The black-dashed lines in (a and b) represent where the line profiles have been obtained. (c) V<sub>CPD</sub> line profiles of PPy NW with de-oxidative and re-oxidative treatments in dark condition obtained from (a and b). The scale bars in (a and b) are 1  $\mu$ m.

## **III.** Relative reactivity of the oxidative treatments

The reactivity of the oxidative treatments was analyzed for PPy NW and Ag NPs attached PPy NW (PPy<sub>AgNPs</sub>NW) and are relatively characterized with the space charge density ( $Q_{sc}$ ) generated near the surface of the PPy NW by the oxidation processes. From the typical equation of the relationship between built-in potential and the depletion region (W),<sup>2</sup>  $Q_{sc}$  can be calculated using the following equation:

$$Q_{sc} = qN_dW = \sqrt{2q\varepsilon_0\varepsilon_r N_d |\Delta V_{CPD,Oxi}|} \quad , \tag{1}$$

where *q* is the elementary charge (~ $1.6 \times 10^{-19}$  coulombs),  $\varepsilon_r$  is the relative dielectric constant of PPy NW (13.6),<sup>3</sup>  $\varepsilon_0$  is the vacuum permittivity (~ 8.85 × 10<sup>-12</sup> F·m),  $N_d$  is the charge density of PPy NW (~ $3.9 \times 10^{17}$  cm<sup>-3</sup>),<sup>4</sup> and  $\Delta V_{CPD,Oxi}$  is difference between the V<sub>CPD</sub> of the samples with the oxidative treatment and with the de-oxidative treatment. Considering  $\Delta V_{CPD,Oxi}$  as a term of the built-in potential in Eq. (1) allows the  $Q_{sc}$  to directly reflect the degree of oxidation in samples (changing the surface potential through oxidation). Figure S3 displays the  $Q_{sc}$  of the samples with oxidative treatments obtained in the PPy NW and the PPy<sub>AgNPs</sub>NW. The  $Q_{sc}$  increases as the time of oxidative treatment by water exposure increases from 30 min to 60 min (Figure S3(a)) and from 60 min to 1 year (Figure S3(b)). In addition, the degree of oxidative treatment by air exposure for 1 day seems similar to that by water exposure for 30–60 min, as shown in Figure S3.



**Figure S3.** Bar graphs of  $Q_{sc}$  calculated from samples with oxidative treatments obtained in (a) PPy NW and (b) PPy<sub>AgNPs</sub>NW.

# IV. Change of the surface potential in *n*-type semiconductor NWs with oxidation treatment

In the case of *p*-type PPy NWs, V<sub>CPD</sub> decreases with oxidation treatment as shown in Figure S4(a–d). A topographic image, V<sub>CPD</sub> mapping images, and the line profiles of the V<sub>CPD</sub> of PPy NW with de-oxidation (vacuum drying for a day) and oxidation (exposure to air for a day) treatments are displayed in Figures S4(a), S4(b and c), and S4(d), respectively. The maximum V<sub>CPD</sub> of PPy NW decreases from approximately 54 mV to 37 mV with the oxidation treatment (Figure S4(d)). Interestingly, *n*-type semiconducting NW (ZnO NW) shows oppositely changing V<sub>CPD</sub> with oxidation treatment, as shown in Figure S4(e–h). A topographic image, V<sub>CPD</sub> mapping images, and line profiles of the V<sub>CPD</sub> of ZnO NW with deoxidation (vacuum drying for one day) and oxidation (exposure to air for one day) treatments are displayed in Figures S4(e), S4(f and g), and S4(h), respectively. The maximum V<sub>CPD</sub> of ZnO NW increases from approximately 85 mV to 155 mV through oxidation treatment (Figure S4(i)). Figure S4(i) displays changing the V<sub>CPD</sub> maximum ( $\Delta$ V<sub>CPD</sub>) in the PPy NW and the ZnO NW. The different values of  $\Delta$ V<sub>CPD</sub> in the PPy NW and the ZnO NW; the respective diameters of the PPy NW and the ZnO NW are 200 nm and 100 nm.

Oxygen works as an electron acceptor when it is adsorbed onto an *n*-type semiconductor (ZnO NW), which leads to a decrease in the electron density at the surface of the ZnO NW. The decreasing electron density at the surface of the ZnO NW creates upward band bending near the surface (extending the depletion region).<sup>5</sup> In the case of upward band bending near the surface of an *n*-type semiconductor, the positive charge density at the surface increases, and the opposite occurs in the downward band bending in *p*-type semiconductors.<sup>2</sup> The opposite changes in the charge density at the surface of *n*-type and *p*-type semiconductors make the PPy NW and ZnO NW show opposite changes in the V<sub>CPD</sub> with oxidation treatment.



**Figure S4.** (a) A topographic image, (b and c)  $V_{CPD}$  images, and (d) line profiles of the  $V_{CPD}$  of PPy NW with de-oxidation (vacuum drying for one day) and oxidation (exposure to air for one day) treatments. (e) A topographic image, (f and g)  $V_{CPD}$  images, and (h) line profiles of the  $V_{CPD}$  of ZnO NW with the de-oxidation and oxidation treatments. The scale bars in (a–c) and (e–f) are 300 nm. The black-dashed lines (b, c, f, and g) represent where the  $V_{CPD}$  line profiles have been obtained. The  $\Delta V_{CPD}$  denotes difference in the  $V_{CPD}$  maximum. (i) Bar graphs of  $\Delta V_{CPD}$  obtained from (d) and (h).

# V. Wavelength-dependent V<sub>CPD</sub> of Ag NP<sub>PPyNW</sub> with oxidation treatment

The wavelength-dependent V<sub>CPD</sub> of Ag NP<sub>PPyNW</sub> with oxidation treatment (exposure to air for a few days) is characterized. Figures S5(a) and S5(b) show SEM and AFM topographic images, respectively, of Ag NPs attached to PPy NW. Measurement of the SEM image was carried out as the last characterization, so the Ag NPs attached to PPy NW look different (they would be bent during pre-experiments). Figures S5(c-f) represent V<sub>CPD</sub> mapping images of the Ag NPs attached to PPy NW in dark, red (650 nm), green (532 nm), and blue (450 nm) light irradiation conditions, respectively. Ag NP<sub>PPyNW</sub> is indicated by the white circles. Figure S5(g) shows the V<sub>CPD</sub> line profiles of Ag NP<sub>PPyNW</sub> obtained from the black dashed lines in Figure S5(c-f). The difference in V<sub>CPD</sub> between Ag NP and PPy NW  $(\Delta V_{CPD}(Ag NP_{PPyNW}))$  are obtained from  $V_{CPD}$  line profiles, which are marked by red doubleheaded arrows in Figure S5(g); it is determined from the averaged V<sub>CPD</sub> PPy NW baseline to the maximum V<sub>CPD</sub> of the Ag NP. Figure S5(h) displays the wavelength-dependent  $\Delta V_{CPD}$ (Ag NP<sub>PPvNW</sub>) as bar graphs. The  $\Delta V_{CPD}$  (Ag NP<sub>PPvNW</sub>) is -10 ± 4 mV, -15 ± 3 mV, -15 ± 2 mV, and -19 ± 4 mV in dark, 650-nm, 532-nm, and 450-nm irradiation conditions, respectively. The  $\Delta V_{CPD}(Ag NP_{PPVNW})$  under LSPR (450-nm irradiation) shows the greatest change compared to the others, which represents a more effective POR process than the oxidation process in Ag NP<sub>PPyNW</sub> in dark, green (532 nm), and red (650 nm) irradiation conditions.



**Figure S5.** (a) A SEM image, (b) an AFM topographic image, and V<sub>CPD</sub> mapping images of Ag NP<sub>PPyNW</sub> with oxidation treatment (exposure to air for a few days) in (c) dark condition, (d) red (650 nm), (e) green (532 nm), and (f) blue (450 nm) light irradiation. The positions of Ag NP<sub>PPyNW</sub> are marked by white circles and the scale bars are 500 nm. The black-dashed lines in (c–f) represent where the line profiles shown in (g) have been obtained. (g) The line profiles of Ag NP<sub>PPyNW</sub> in dark, 650-nm, 532-nm, and 450-nm irradiation conditions were obtained in (c–f) of V<sub>CPD</sub> in dark, 650-nm, 532-nm, and 450-nm Ag NP<sub>PPyNW</sub>. The gray dotted line in (g) indicates the middle of the Ag NP<sub>PPyNW</sub>, and the red double-headed arrows denote  $\Delta V_{CPD}$ (Ag NP<sub>PPyNW</sub>). (h) Bar graphs of the wavelength-dependent  $\Delta V_{CPD}$ (Ag NP<sub>PPyNW</sub>) with oxidation treatment.

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