Supporting information

Spatial Distribution of Reaction Active sites for Plasmon-Induced Chemical Reactions Triggered by Well-Defined Plasmon Modes

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1. Electrochemical measurements of each monomer molecule

Cyclic voltammograms for pyrrole, BT, EDOT, DT, MT, and thiophene molecules were obtained for the determination of the oxidation potentials. The electrochemical potential was scanned to the anodic direction (shown as the red arrows), then, the potential was returned to the cathodic direction (blue arrows). The broken lines are corresponding to the oxidation potential for each monomer as described in the main text.



Figure S1. Cyclic voltammograms of FTO electrodes immersed in the acetonitrile electrolyte solutions containing 0.1 M NaClO₄ and (a) 10 mM pyrrole, (b) 10 mM BT, (c) 10 mM EDOT, (d) 10 mM DT, (e) 100 mM MT, and (f) 100 mM thiophene. The potential scan rate was set to 50 mV s⁻¹.

2. Finite-difference time-domain calculations for each rod length

The spatial distributions of the excited electric field under the illumination of $\lambda_{ex} =$ 785 nm has been examined through the finite-difference time-domain (FDTD) calculations. Figure S2 shows the results for each results of each FDTD calculation. The substrate was TiO₂ and the spatial distribution indicate the interface between the Au and TiO₂.



Figure S2. FDTD calculations for each Au rod structure as in Fig. 3. Each rod length was set to (a) 75, (b) 300, (c) 550, and (d) 750 nm, respectively. All Au rod structures were deposited on TiO_2 substrate. The results are corresponding to the interface between Au and substrate.

3. Deposition of polypyrrole on each Au rod structure by transverse mode excitation Figure S3 shows the deposited polypyrrole on each Au rod structure. The polarized direction of the incident light was indicated as the double head arrows on each figure. Unlike the results in Fig. 3, the polypyrrole deposited on the entirely surface of the Au rod structures in all cases. This is due to the spatial distribution of the electric field for the transverse mode of rod structures.



Figure S3. SEM images of Au nanorods after irradiation of polarized laser with 0.1 mW of 785 nm. The rod length and irradiation time were (a) 75, (b) 300, (c) 550, and (d) 750 nm, respectively. The laser irradiation was conducted in 1 mM pyrrole + 0.1 M NaClO₄ acetonitrile solution at the static potential of 0.3 V vs. Ag/Ag^+ . The double-headed arrows shown in each image indicate the polarization direction of incident light and the laser exposure time was set to 10 sec.