Supporting Information

Electrocatalytic glycerol oxidation enabled by surface plasmon polariton-induced hot carriers in Kretschmann configuration

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Computational Detail

The calculations were carried out on the basis of spin-polarized density functional theory (DFT) within the Perdew–Burke–Ernzerhof (PBE) [1], as implemented in the Vienna Ab-initio Simulation Package (VASP)[2]. The projector augmented wave (PAW) method using a plane wave basis set [3] was accepted to describe the interaction between core and valence electrons. An energy cutoff of 400 eV was used for the plane wave expansion of the electronic eigenfunctions. The equilibrium lattice constant for bulk Au was calculated to be 4.16Å, which is similar to the previous calculation value of 4.18Å [4]. For modeling Au catalyst, we used the 4 × 4 hexagonal Au(111) slab with the four atomic layers. The bottom two layers of the four-layered slab are frozen at the equilibrium bulk lattice constant, while the upper three layers are fully relaxed using the conjugate gradient method until residual forces on all the atoms become smaller than 0.05 eV/Å. The slab was separated from its periodic images in the vertical direction by a vacuum space corresponding to eight atomic layers. For the Brillouin zone integration [5], we used a 2 × 2 × 1 Monkhorst–Pack mesh of k points to predict optimized geometries and total energies. To examine the light-induced hole effect on the catalytic activity of Au catalyst, we have calculated the Gibbs free energy for the glycerol oxidation at the alkaline condition by reducing the number of electrons in the Au(111) slab. The Gibbs free energy is calculated by using the following equation.

$$\Delta G = \Delta H_{DFT} + \Delta ZPE - T\Delta S + kT \times \ln 10 \times pH \qquad (1)$$

where $\Delta H_{DFT,}$ ΔZPE, and ΔS are the energy change obtained from DFT calculation, zero-point energy, and entropy, respectively. The entropy and zero-point energy can be estimated by using the following equations [6].

$$S = k \sum_{i}^{\#\ of\ modes} \left\{ \frac{x_i}{e^{x_i} - 1} - \ln\left(1 - e^{-x_i}\right) \right\} \qquad (2)$$

$$x_i = \frac{hv_i}{kT} \qquad (3)$$

$$ZPE = \sum_{i} 0.5 hv_i \qquad (4)$$

where k, h and x_i is the Boltzmann constant, Planck constant and vibrational mode in terms of vibrational frequency, v_i, respectively.

Figure S1. Scanning electron microscope (SEM) images of bare Au film (a-b) and AuNBP@AgPt-coated Au film (c-d), before and after 10000 cycles of CV measurements of glycerol electro-oxidation.

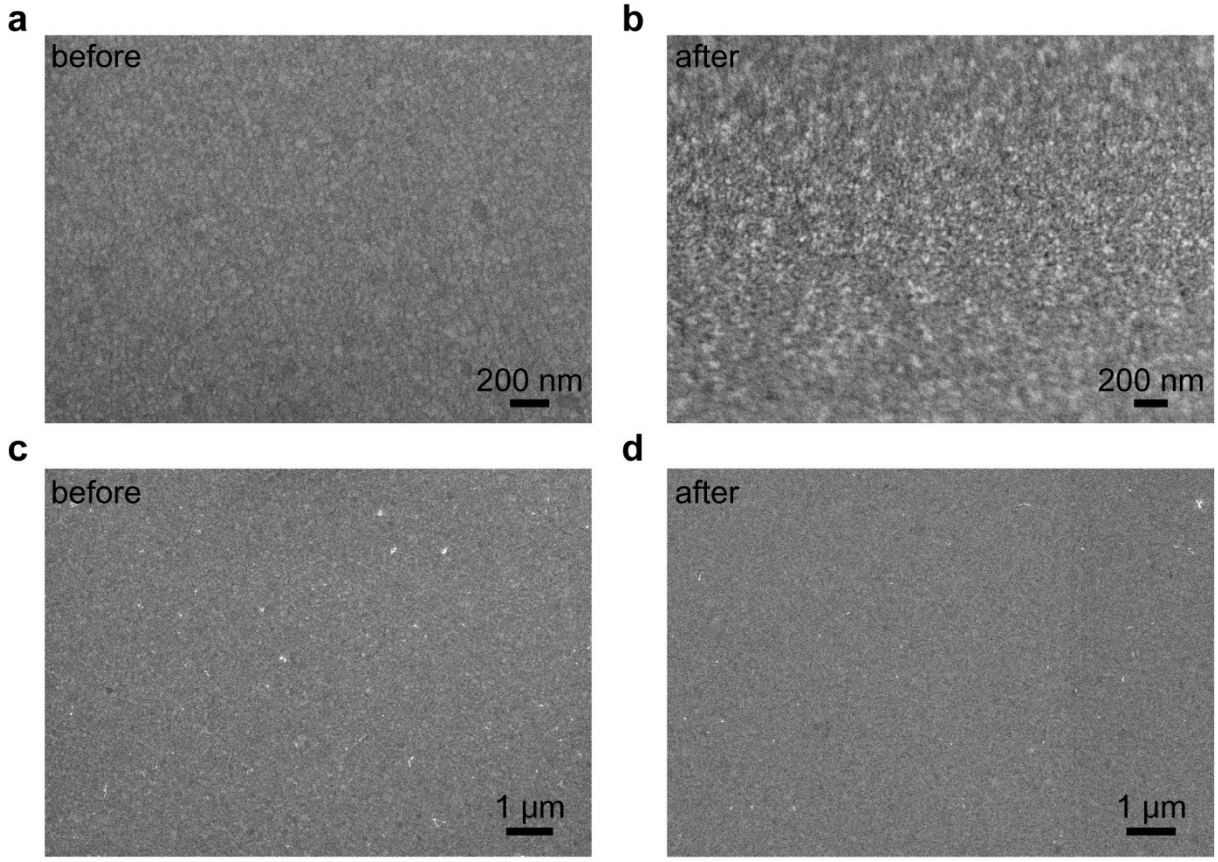


Figure S2. Illustration of (a) AuNBP with Pt nanoparticles (diameter 3 nm) at tip ends deposited on Au film without any spacing for FDTD simulation. Electric field (E_y component) distribution with low magnification view of bare Au film (b) and AuNBP with Pt nanoparticles deposited on Au film (c), respectively.

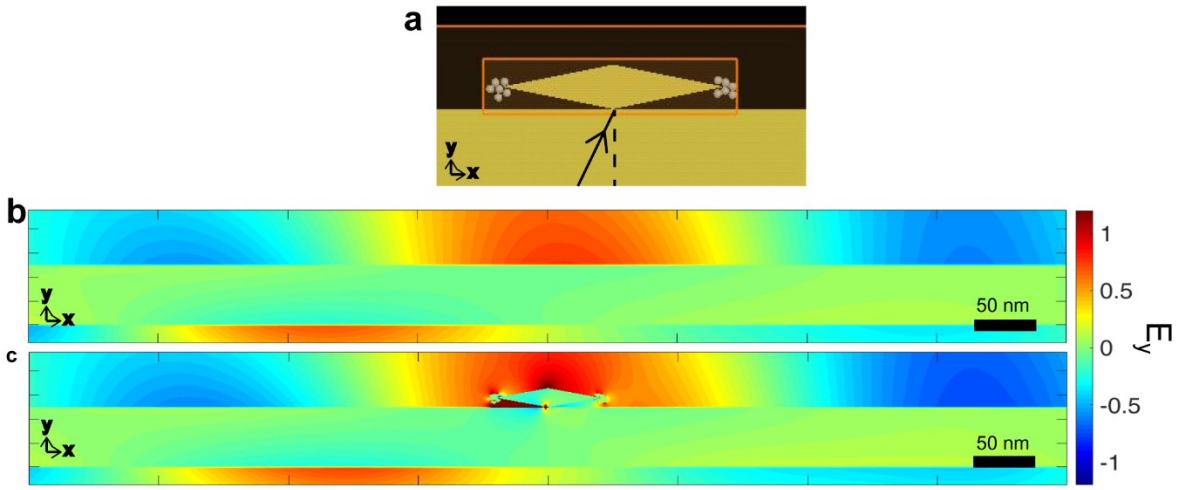


Figure S3. Schematic diagram of the electrochemical SPR setup.

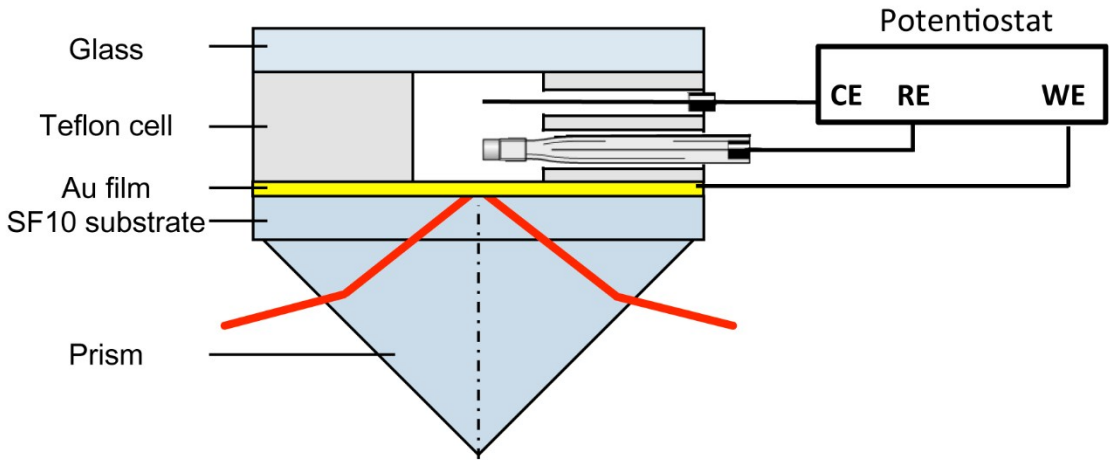


Figure S4. Parallel beam X-ray diffraction patterns of of bare Au film and AuNBP@AgPt-coated Au film, before and after 10000 cycles of CV measurements of glycerol electro-oxidation.

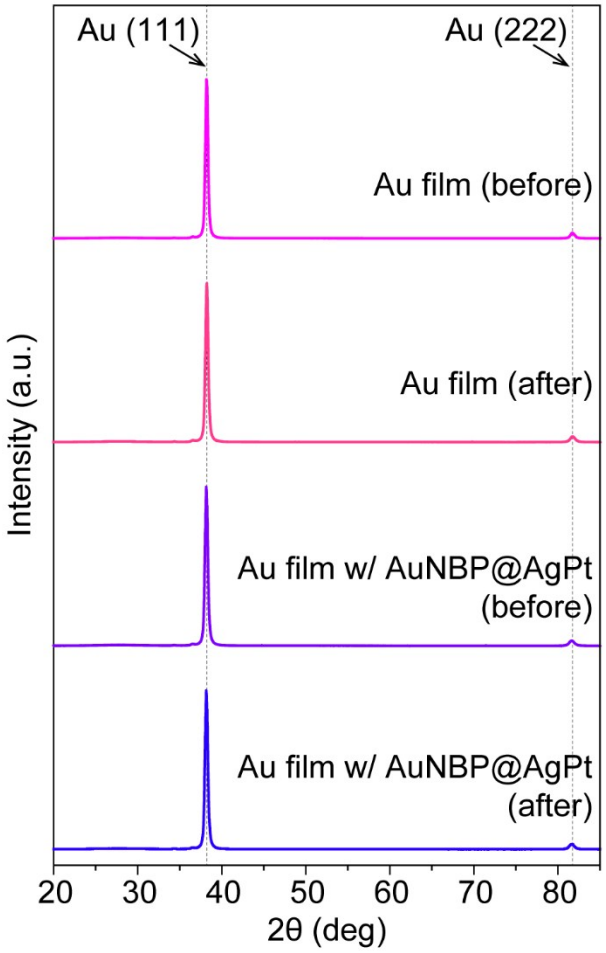


Table S1. XRD peak position and full width at half maximum (FWHM) of Au(111) from bare Au film and AuNBP@AgPt-coated Au film, before and after 10000 cycles of CV measurements of glycerol electro-oxidation.

	Au film (before)	Au film (after)	Au film w/ AuNBP@AgPt (before)	Au film w/ AuNBP@AgPt (after)
2θ (deg)	38.21	38.22	38.17	38.17
FWHM (deg)	0.40	0.44	0.43	0.43

Figure S5. Cyclic voltammograms of a) bare Au film and b) 10 nm TiO_2-deposited Au film in an aqueous solution of 5 mM $K_3Fe(CN)_6$ in 0.1 M KCl solution with or without illumination at resonant angle (scan rate: 100 mV/s).

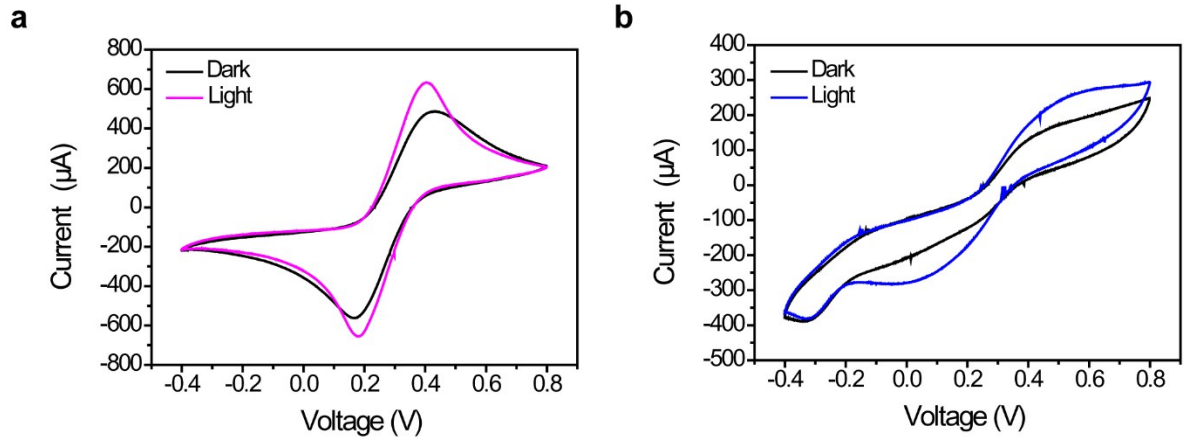
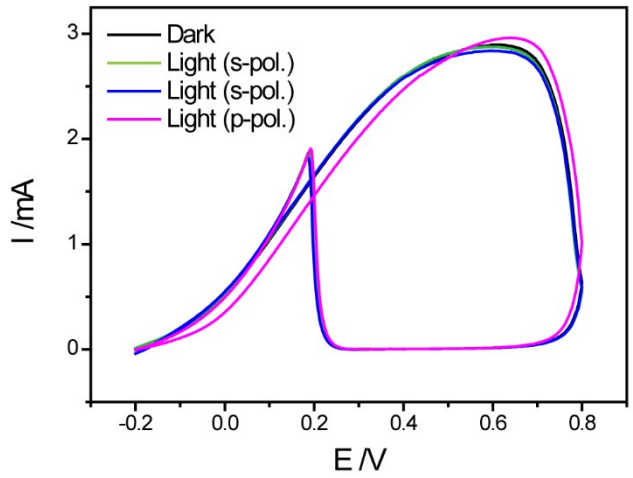


Figure S6. Cyclic voltammograms of glycerol oxidation without or with illumination at resonant angle (*s*- and *p*-polarized light) using bare Au film. To confirm the effect of *p*-polarized illumination, CV curves at *s*-polarized illumination were repeated two times.



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