Electronic Supplementary Material (ESI) for Nanoscale.

Surface Plasmon Polariton-Induced Hot Carrier Generation for Photocatalysis

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Supporting Information

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Photon-to-Hot Carrier Conversion Efficiency Calculation. We calculated the photon-to-carrier conversion efficiency, η, by taking the ratio of photocurrents measured by our working electrodes (electrons per second) to the number of photons incident on the half-ball lens per second. Photocurrents measured in Ampere (Coulombs per second) from the electrochemical cell were first converted to electrons per second by converting Coulombs to electron charge as 1 e = 1.602 x 10^{-19} C. The illumination laser power measured by a power meter in Watts was converted to photons per second by dividing the power (Joules per second) by photon energy (E, Joules per photon). The photon-to-hot carrier conversion efficiency was then calculated according to Eq. S1 and listed in **Table S1** for different metal films and lasers.

$$\eta = \frac{Photocurrent\ (electrons/sec)}{Illumination\ Intensity\ (photons/sec)} \times 100 \qquad \text{(Eq. S1)}$$

Table S1. Photon-to-hot carrier conversion efficiency.

Working electrodes	Laser (nm)	Laser power (W)	Current (A)	Efficiency (%)
Ag/TiO_2	785	$3.2x10^{-3}$	$1.4x10^{-11}$	$7.0x10^{-7}$
		$3.3x10^{-2}$	$2.6x10^{-11}$	$1.2x10^{-7}$
	532	$2.1x10^{-6}$	$4.0x10^{-11}$	$4.7x10^{-3}$
		$1.3x10^{-5}$	$6.2x10^{-10}$	$1.1x10^{-2}$
		$2.3x10^{-5}$	$8.4x10^{-10}$	$8.4x10^{-3}$
Au/TiO_2	785	$1.4x10^{-2}$	$2.5x10^{-11}$	$2.9x10^{-7}$
		$1.3x10^{-2}$	$2.5x10^{-11}$	$3.1x10^{-7}$

Estimation of a Temperature Increase through Plasmonic Heating. Although the linear dependence of photocurrent on illumination power is a clear indication of a photocarrier-driven process, we further substantiate this assignment by calculating the maximum temperature increase the system could possibly experience. Heating of the face of a metal slab by laser irradiation follows[1]

$$\Delta T = \frac{H}{k}\sqrt{\frac{4\alpha t}{\pi}} \qquad \text{(Eq. S2)}$$

where ΔT is the temperature rise, H is the absorbed laser energy, k is the thermal conductivity of gold (310 $^{W}/_{m*K}$), α is the thermal diffusivity (3.2×10^{-5} $^{m^2}/_{s}$ for a 50 nm thin film)[2] and t is time. Making the most generous assumptions to maximize temperature rise (*e.g.*, inserting the highest laser power used in this study, 33 mW, and assuming that *all* laser energy is absorbed in the film and that energy does not dissipate from the slab), results in a calculated rise of <1 °C for the illumination times used. Simply reducing the inserted laser power to that used for the majority of experiments reduces this predicted temperature increase by an order of magnitude and properly considering only partial photon absorption as well as heat dissipation into solution would decrease this temperature rise even further. These calculations confirm that heating is not responsible for the electrochemical responses presented in this work.

Tunneling Probability. Estimates of tunneling probability can be calculated according to the following expression.[3]

$$T_t = \frac{16E(E_0 - E)}{{E_0}^2} exp\left(-2W \sqrt{\frac{2m^*(E_0 - E)}{\hbar^2}} \right) \quad \text{(Eq. S3)}$$

T_t is the tunneling probability, E the energy of the carrier, E_0 the barrier height, W the barrier width, m^* the effective mass of the tunneling carrier ($0.8*m_e$ for holes in TiO_2)[4] and $\hbar$ is Planck's constant. If one assumes the only state available to accept a tunneling hole from the metal is located 0.4 eV below the Fermi level (this is the redox potential of the OH oxidation reaction), the tunneling probability is ~10^{-59} due primarily to the large (~2.2 eV) and somewhat thick (10 nm) barrier. Even if one assumes the carriers may tunnel into a continuum of states spanning the entire region below the Fermi level and considering the most highly excited holes possible (~0.3 from the TiO_2 valence band), tunneling probability is still only ~10^{-22}. Therefore, even for the most energetic carriers created in this study, tunneling is negligible.

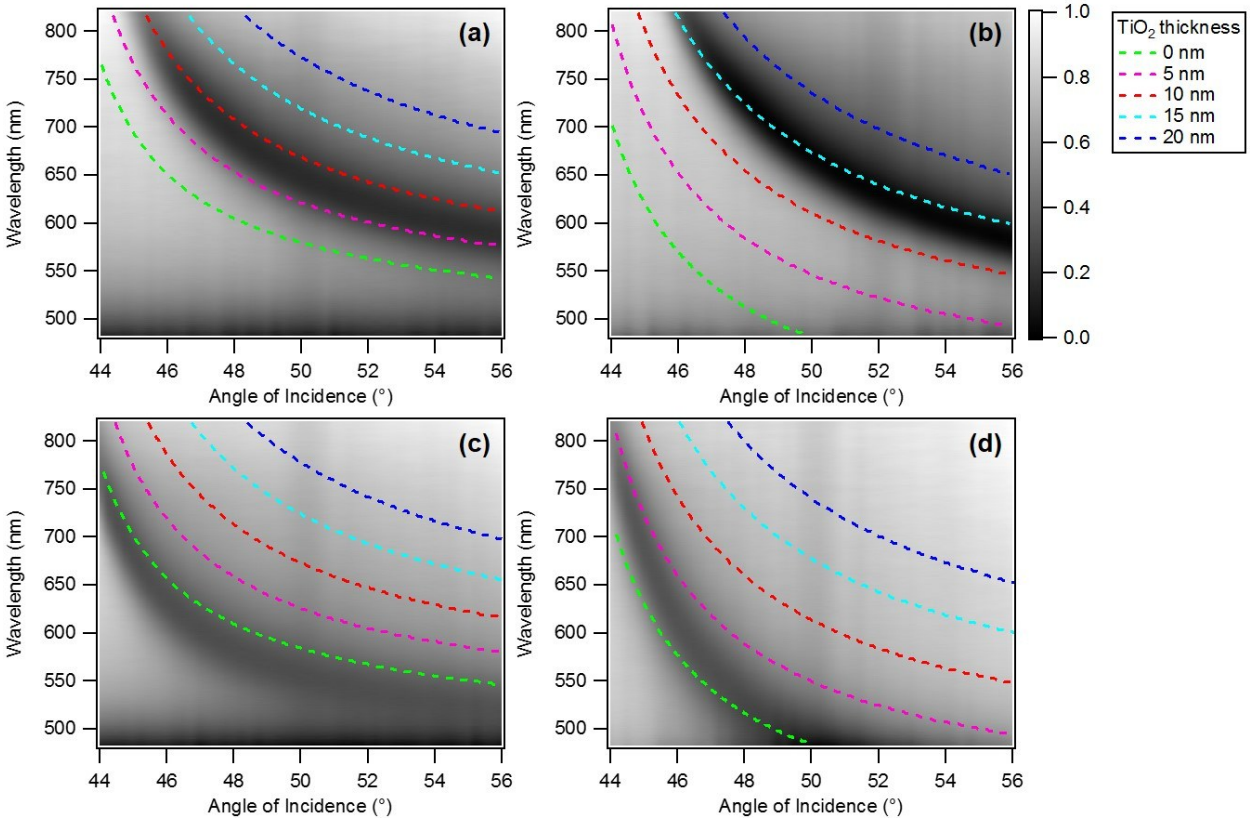

Figure S1. SPP dispersion curves. Measured SPP dispersion curves (black and white contour) for (a) Cr/Au/TiO_2 (2/40/10±5 nm), (b) Cr/Ag/TiO_2 (2/40/10±5 nm), (c) Cr/Au (2/40 nm), and (d) Cr/Ag (2/40 nm) are overlaid with simulated dispersion curves (color dashed lines) with varying TiO_2 thicknesses.

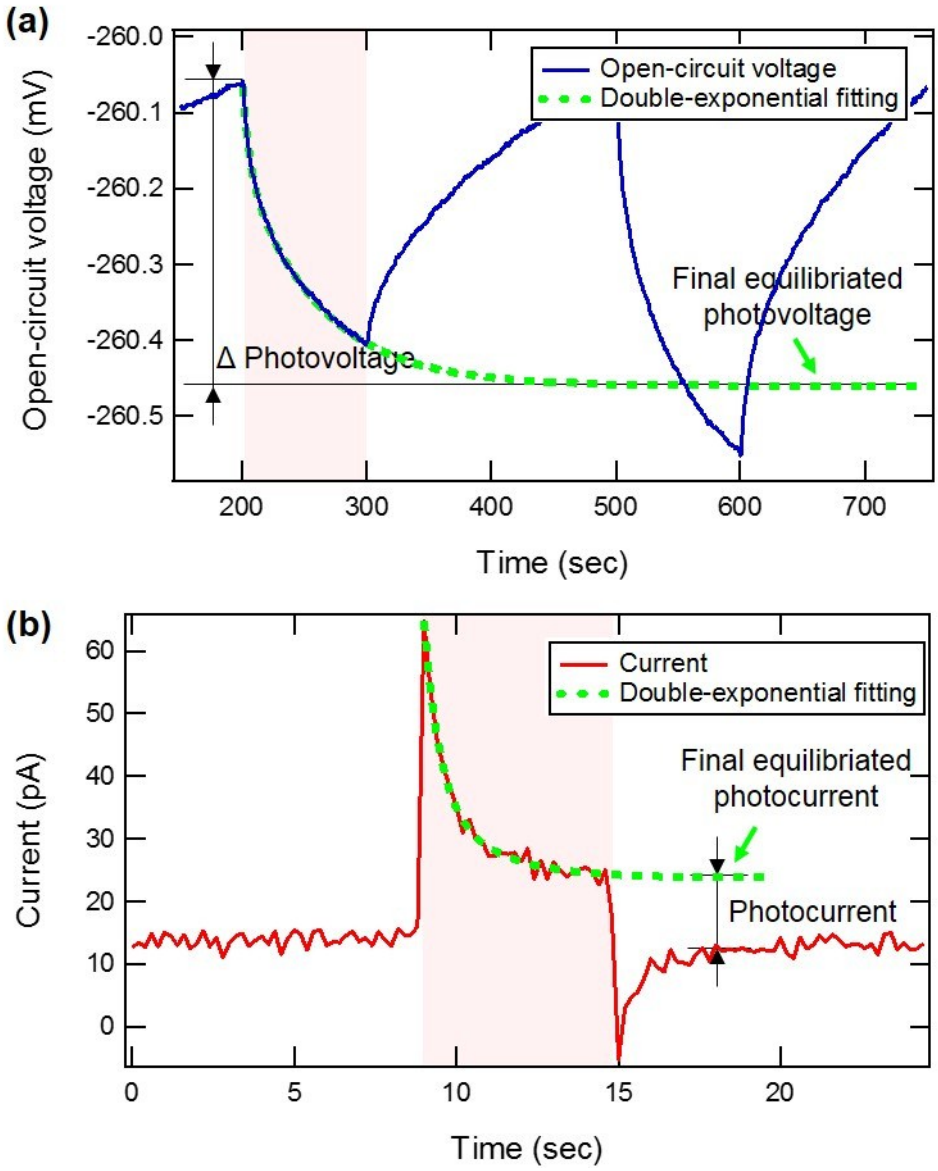

Figure S2. Data processing for photovoltage and photocurrent responses. A double-exponential function was fitted to the light irradiated regions (red shades) of (a) open-circuit voltage and (b) current curves to obtain the final equilibrated values (green dash lines) and Δ values (black arrows).

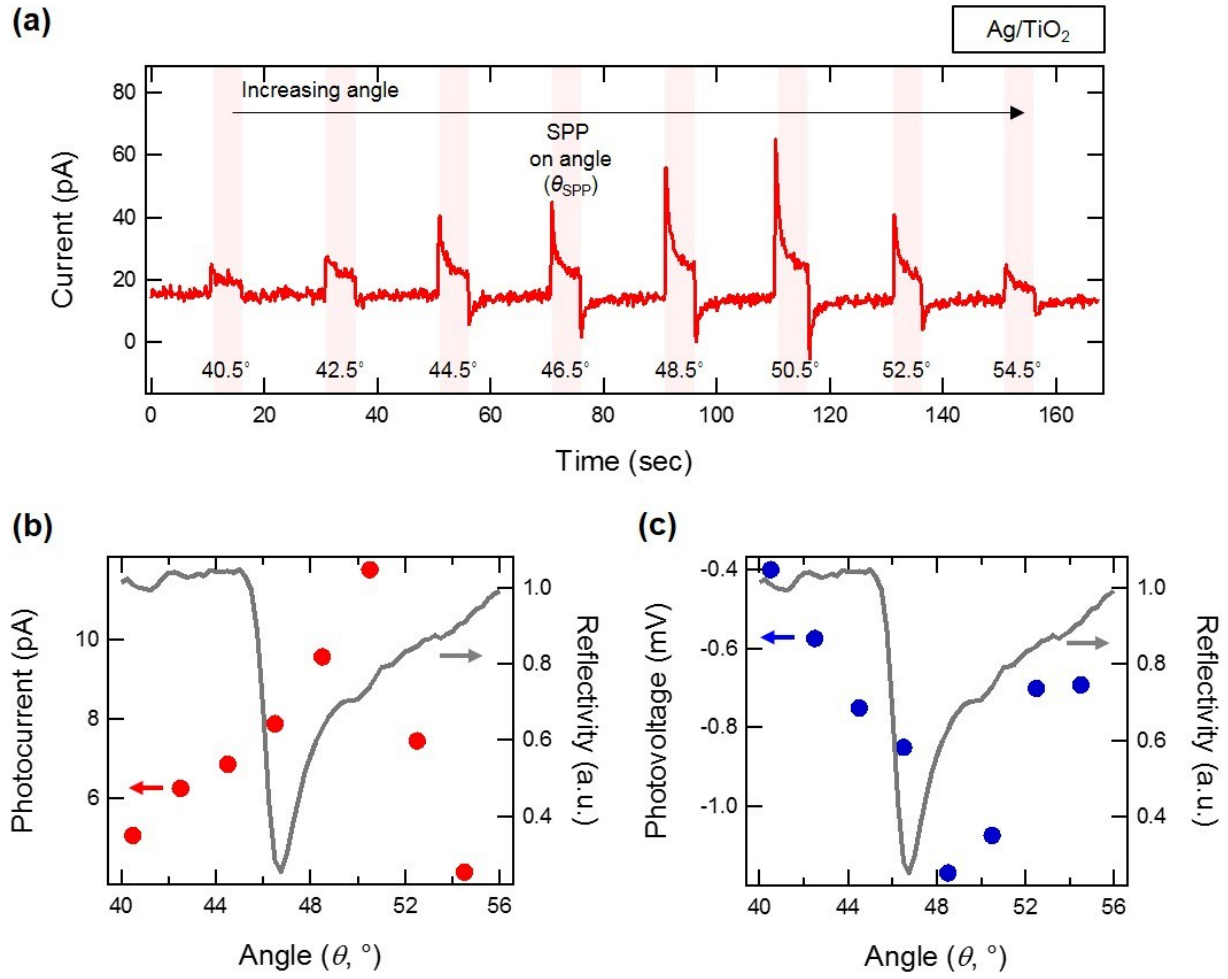

Figure S3. Anodic half-reaction of photocatalytic water-splitting. A Ag/TiO_2 deposited half-ball lens was in contact with methanol-free sodium hydroxide solution (0.1 M) and illuminated with 785 nm laser (red shaded regions). (a) Dependence of current on the incident angle of light. Angle dependent photocurrent (b) and photovoltage (c) plotted with a SPP resonance spectrum at 785 nm (gray line). A small positive bias of 0.20 V was applied during the current measurement.

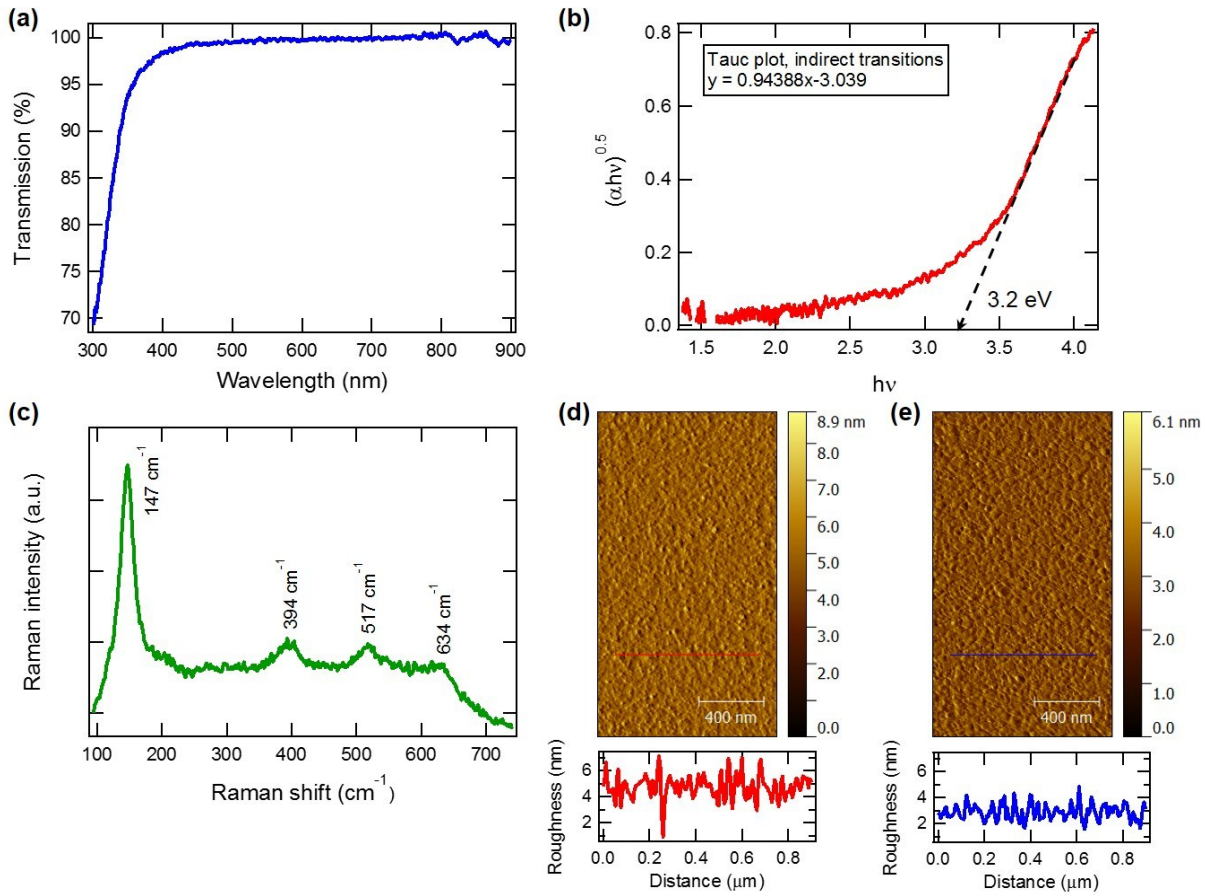

Figure S4. Characterization of ALD grown TiO_2 films. (a) % transmission of a 10 nm thick TiO_2 layer approaches ~100% above λ = ~390 nm, from which a band gap (E) of the TiO_2 film can be calculated as 3.2 eV using an equation, $E = hc/\lambda$, where h is Plank's constant and c is speed of light. The calculated band gap agrees well with results from the Tauc plot (b) that extrapolates a band gap of the ALD grown TiO_2 to 3.2 eV, which is a band gap of anatase TiO_2. (c) Raman spectrum of a TiO_2 layer (~70 nm thickness, on top of Cr/Au, 2/40 nm thickness) also indicates that the TiO_2 films that we grow by ALD have an anatase crystalline structure, showing anatase characteristic Raman peaks.[5] It is known that peaks at 147 and 634 cm^{-1} are by symmetric stretching vibration of O-Ti-O, a peak at 394 cm^{-1} is by symmetric bending vibration of O-Ti-O, and a peak at 517 cm^{-1} is by antisymmetric bending vibration of O-Ti-O.[6] Atomic force microscope images and cross-section profiles show that ALD grown TiO_2 on top of Cr/Au films (d) has ~2 nm increased roughness than TiO_2-free Cr/Au (e).

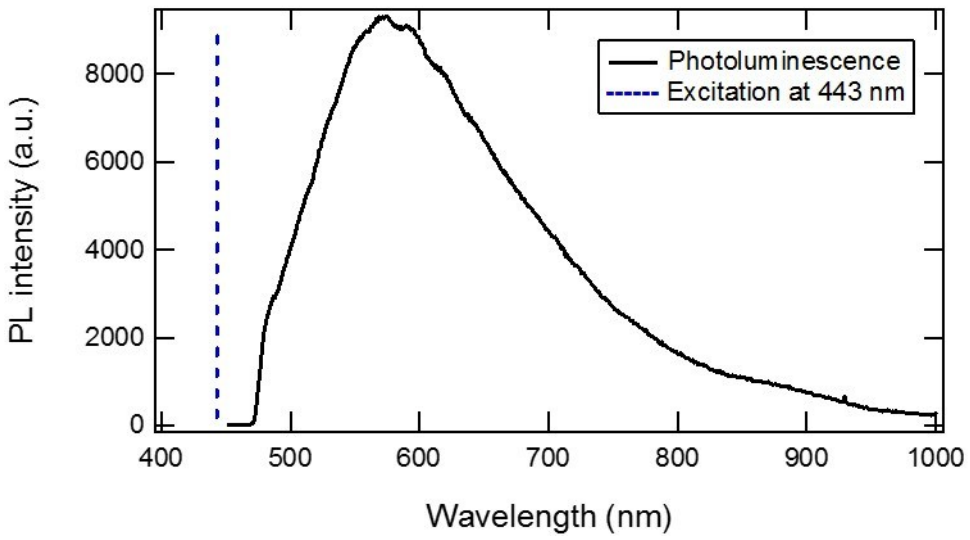

Figure S5. Photoluminescence from a TiO_2 layer. PL intensity was acquired from ~70 nm thick TiO_2 film grown by ALD on top of Cr/Au (2/40 nm thickness) on a glass substrate. A 443 nm laser (blue dash line) was used as an excitation source with 460 dichroic and 480 nm long pass filters.

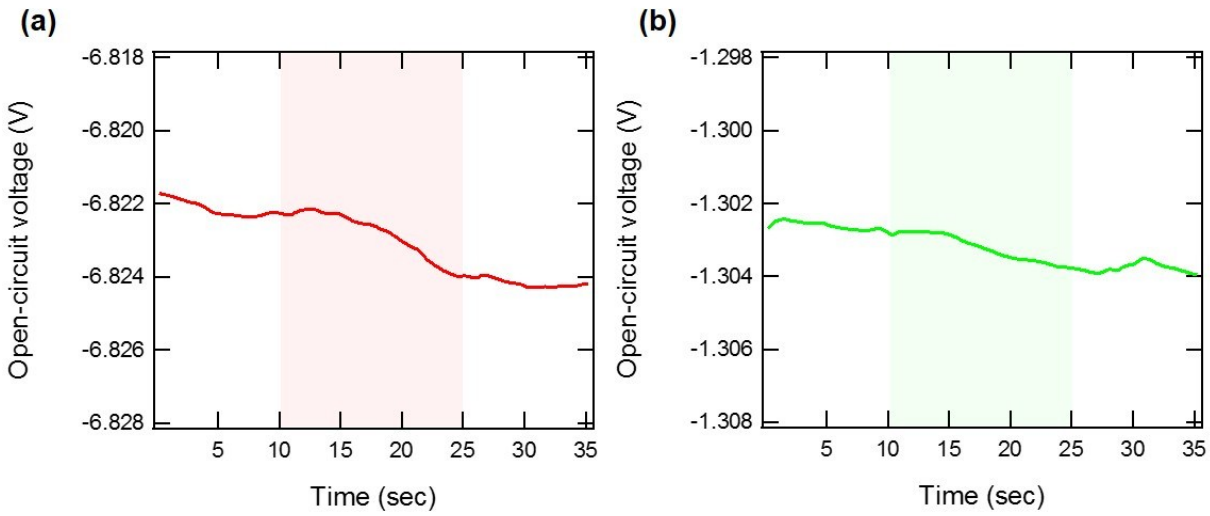

Figure S6. Open-circuit voltage of a bare TiO_2 film. A TiO_2 film in the absence of the metal film showed no light-induced photovoltage responses upon (**a**) 785 and (**b**) 532 nm laser irradiation (red and green shaded regions, respectively).

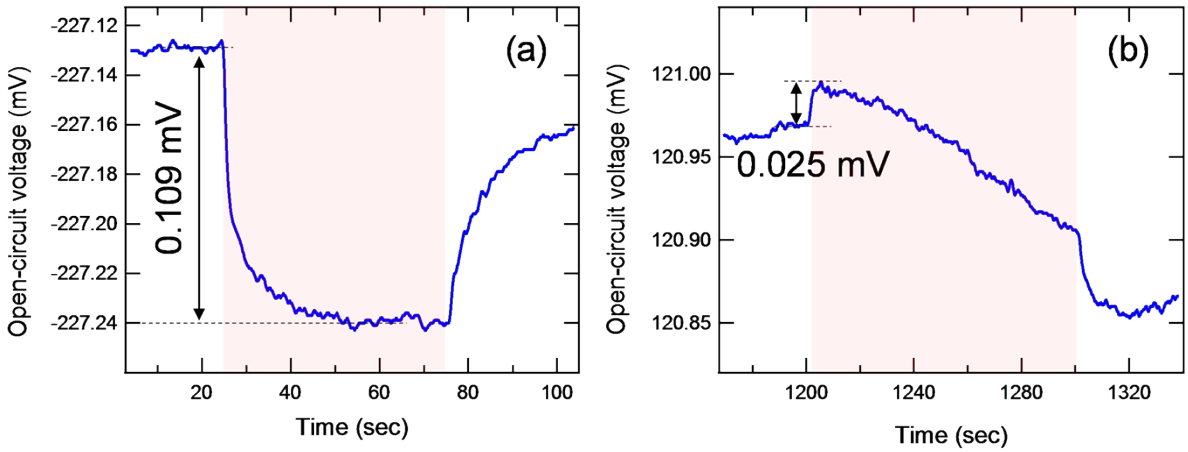

Figure S7. Open-circuit voltage versus time profiles of (a) Au/TiO_2 and (b) Au only system. A 785 nm laser (red shades) was incident on each system at their SPP resonant angles.

References

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