Supporting Information

Water Oxidation under Modal Ultrastrong Coupling Conditions Using Gold/Silver Alloy Nanoparticles and Fabry–Pérot Nanocavities

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S1. Experimental procedures

Fabrication of Au-Ag alloy NP/TiO$_2$/Au film substrates: Silica glass substrates with a size of $10 \times 10 \times 0.5$ mm$^2$ were sequentially rinsed with acetone, methanol and deionized water in an ultrasonic bath for 3 min and then dried with an air flow. A 2 nm titanium film, a 100 nm Au film, and a 2 nm titanium film were sequentially sputtered on the surface of silica glass using a Helicon sputter (ULVAC, MPS-4000C1/HC1). Titanium dioxide thin films were deposited onto the Au film using a commercial hot-wall flow-type atomic layer deposition (ALD) reactor (SUNALETM R series (Picusron)) with titanium tetrachloride (TiCl$_4$) and H$_2$O as precursors; the chamber was held at 300°C. A quadruple layer of Au, Ag, Au, and Ag films with different film thicknesses (0.8 nm Ag, 1.8 nm Au, 0.7 nm Ag, and 1.7 nm Au) was sequentially evaporated by a thermal evaporator at a deposition rate of 0.2 Å s$^{-1}$. Subsequently, the samples were annealed in a nitrogen atmosphere at 400°C for 10 h, and Au-Ag alloy NPs were formed on the TiO$_2$ film surfaces. To remove the silver oxide on the surface of Au-Ag alloy NPs, the samples were submerged in a 19 wt% NH$_3$ aqueous solution for 3 min. Immediately after that, a 7 nm TiO$_2$ thin layer was additionally deposited on the Au-Ag alloy NP/TiO$_2$/Au film by ALD to fabricate partially inlaid Au-Ag alloy NPs.

Material characterization: The reflection spectra were measured by a spectrophotometric reflectometer (F20-UV (Filmetrics)). The surface morphology was observed by field-emission SEM (JSM-6700FT (JEOL)) with a maximum resolution of 1 nm at an electron accelerating voltage of 15 kV. The cross-section was analysed by high-resolution transmission electron microscopy (JEOL ARM (200 F) 200 kV FEG-STEM/TEM) with a resolution of 75 pm at an electron accelerating voltage of 200 kV. The EDS elemental mapping image of alloy NPs was obtained by using TEM with energy dispersive analysis. Samples for TEM and EDS were made by the focused ion beam technique (JEOL JIB-4600F/HKD) with Ga ions accelerated at a voltage of 30 kV. The photoelectron detection performance was measured using ultraviolet photoelectron spectroscopy (AC-3, Hitachi High-Tech). The work function was derived from the intersection of the ground level and the straight line extrapolated from the slope of the graph of the irradiated light energy and photoelectron yield obtained by the least-squares method.

Photoelectrochemical measurements: An InGa alloy (4:1 weight ratio) film was attached onto the Au thin film and then connected to an electrochemical analyser (ALS/CH Instruments 852 C (ALS)) with a copper lead wire. A KOH (0.1 mol dm$^{-2}$) aqueous solution was used as the supporting electrolyte solution. An 800 W xenon lamp was used as the light source. For measurements of the IPCE spectra and current–voltage curves, a standard three-electrode system was employed with a platinum wire and a Ag/AgCl electrode as the counter electrode (CE) and reference electrode (RE), respectively. The Au-Ag alloy NP/TiO$_2$/Au film working electrode potential was set to +0.5 V vs Ag/AgCl to obtain the constant–time characteristics by bandpass filters with a bandwidth of less than 15 nm.

O$_2$ evolution measurements: For O$_2$ evolution measurements, two platinum wires were employed as the CE and RE. Xenon light spectrally filtered over a wavelength range of 400–900 nm was used as the light source, and a 0.5 V bias was applied during the photoelectrochemical water-oxidation measurements. The O$_2$ evolution was quantified by mass spectrometry (GC-MS 2010 plus (Shimadzu)). A KOH aqueous solution with $^{18}$O water (16.2 atom% isotopic purity) was used to quantify the O$_2$ evolution. The Faraday efficiency for O$_2$ evolution was calculated using the following equation.

$$\text{Faraday efficiency} (\%) = \frac{F(Q_{\text{ev}})}{Q_{\text{total}}} \times 100$$

where $[O_2]$ is the concentration of evolved O$_2$ molecules, $F$ is the Faraday constant, 96485 C mol$^{-1}$, and $Q_{\text{total}}$ is the total charge passed during the reaction.

Transient absorption measurements: A double-beam Ti:sapphire laser was built for transient absorption measurements in reflection mode by a pump-probe method. The fundamental output from a regenerative amplified Ti:sapphire laser (800 nm femtosecond pulses with a repetition rate of 1000 Hz and a pulse duration of 25 fs) was divided into two beams that served as pump and probe pulses. For the pump pulse, the pulse was input into a collinear optical parametric amplifier (Light Conversion, TOPAS-C) and chopped at 500 Hz to supply tunable visible excitation with an identical pulse energy of 1 mW. For the probe pulse, a noncollinear difference frequency generator (NDFG) was employed to provide a 3500 nm probe pulse. The delay time between the pump and probe pulses was controlled by a linear stepper stage. Both the pump and probe pulses were guided to the sample by concave mirrors with a loose focus, where the pump pulse was normally incident, while the probe pulse was set to oblique incidence. The reflection signal was collected and detected by a liquid nitrogen-cooled mercury cadmium telluride (MCT) detector. The absorbance values of the transient signals were obtained from the signals with and without a pump pulse. For data analysis, the following second-order kinetics signal was used to fit the electron–hole recombination kinetics.$^{[1]}$

$$\% \text{absorption} = \frac{a[C_0]}{k_r[C_0] + \text{const}} + \text{const}$$

where $[C_0]$ and $k_r$ refer to the initial concentration of photogenerated carriers, and a second-order rate constant for electron–hole recombination, respectively. The coefficient $\alpha$ is dependent on the extinction coefficient of photogenerated carriers and the scattering coefficient of the surface of the sample.
S2. Peak separation and assignment of the FP nanocavity resonance

Figure S1. Absorption spectra of TiOx/Au films with TiOx thicknesses of 28 nm (a), 35 nm (b), 140 nm (c), and 150 nm (d) (black curves), and peak separation in the absorption spectrum based on Lorentzian fitting. Because the cavity mode and the interband transition of the Au film overlap, the peak energy of the cavity mode was analysed by using the peak separation based on Lorentzian fitting. The resonant wavelength of the nanocavity mode (red curves) was obtained from the fitted absorption spectrum.
S3. Morphology of Au-Ag alloy NPs

Figure S2. SEM image of AATA with a Au-Ag alloy NP inlay depth of 0 nm.
**S4. Estimation of the splitting energies of AATA with partially inlaid Au-Ag alloy NPs**

Figure S3. Dispersion curves of hybrid modes in AATA (a) and ATA (b) with TiO$_2$ thicknesses of 21 nm and 28 nm and Au-Ag alloy NP and Au NP sizes of 20 nm and 12 nm, respectively. The Au-Ag alloy NPs and Au NPs were partially inlaid in the nanocavity at an inlay depth of 7 nm. The red curves show the fitting using a coupled harmonic oscillator model. The blue dashed line shows the LSPR energy of the Au-Ag alloy NPs and Au NPs. The cyan dashed line displays only the cavity mode of a TiO$_2$/Au film.
S5. Stability of the AATA photoanode

The oxidative elution of Ag should be prevented for application of the AATA photoanode to water oxidation. We monitored the absorption spectra after different light irradiation times in the photoelectrochemical measurements because the elution of Ag changes the LSPR wavelength, resulting in modulation of the energies of the hybrid modes (Figure S4a). This experiment was carried out in a three-electrode system using an AATA photoanode as the working electrode and a KOH (0.1 mol dm$^{-3}$) aqueous solution as the electrolyte. This photoanode was irradiated with monochromatic light of 580 nm, which is the wavelength with the highest IPCE, for 3 hours, and the optical characteristics were measured for each irradiation time. A redshift in the optical spectrum was observed up to 1 hour, and then, almost no change in the spectrum was observed after that. Thus, the elution of silver was confirmed to stop in approximately 1 hour. The spectral change is due to the change in the tuning of the coupling condition because the resonance peak of the LSPR was blueshifted from 618 nm to 595 nm by the light irradiation. Additionally, no significant change was observed in the shape of the Au-Ag alloy NPs, although the particle size slightly shrank from 21 to 20 nm (Figure S4b). Therefore, Ag remained inside the Au-Ag alloy NPs without elution.

Figure S4. a) Absorption spectra of AATA with partially inlaid Au-Ag alloy NP structures for various light irradiation times under the photoelectrochemical measurement setup using a three-electrode system. The TiO$_2$ thickness was 21 nm. The alloy NP inlay depth was 7 nm. The wavelength of the irradiation light was 580 nm. b) SEM images of AATA with partially inlaid Au-Ag alloy NPs at light irradiation times of 0 min and 180 min. A KOH (0.1 mol dm$^{-3}$) aqueous solution was used as the supporting electrolyte solution. c) Current-time curves for the AATA photoanode corresponding to (a).
S6. Detailed analysis of the transient measurement

The instrument response function (IRF) of our system was estimated using a similar method as described in our previous report.\textsuperscript{[2]} Briefly, we measured the transient signal of a Si wafer under a 600 nm pump and a 3500 nm probe, as shown in Figure S5a. The time resolution of this system was estimated to be ~250 fs, which was obtained through fitting of the rising edge of the transient signal associated with the formation of free charge carrier in the Si substrate.

The IRF was convolved with a second-order reaction model, as described in Supporting Information S1. The maximum $\Delta$OD for each measurement was estimated by extracting the maximum value of the fitted convoluted function that occurred near time zero, i.e., temporal overlap between the pump and probe pulses. The fitting and $\Delta$OD$_{\text{max}}$ values are depicted in Figure 3 in the main text. The wavelength dependence of $\Delta$OD$_{\text{max}}$ showed a similar tendency as the IQE action spectra in Figure 2d. In the case of AATA, the shorter wavelength corresponding to the upper branch of the hybrid state showed very high IQE and $\Delta$OD$_{\text{max}}$ due to the efficient electron injection, as discussed in the main text. Additionally, in the case of ATA, the wavelength dependences of the IQE and $\Delta$OD$_{\text{max}}$ were flatter than those of AATA.

Additionally, we determined the second-order rate constant $k_r$ from the fitting. The $k_r$ values of AATA and ATA are summarized in Figure S5b. The average $k_r$ values of both AATA and ATA are almost the same (1.3 dm$^3$ mol$^{-1}$ ps$^{-1}$). This result suggests that the decay processes of the injected electrons in the TiO$_2$ of AATA and ATA are similar.

**Figure S5.** (a) Transient signals of a Si plate with a pump wavelength of 600 nm (0.25 mW) and a probe wavelength of 3500 nm, shown as $\Delta$OD vs the pump-probe delay time. (b) $k_r$ of AATA and ATA for different wavelengths. The data at 720 nm are not shown because the signal intensity of ATA was too weak.
Figure S6. Relationship between UV energy and photoelectron yield obtained by ultraviolet photoelectron spectroscopy. The photoelectric work function is derived from the intersection of the ground level and the straight line extrapolated from the slope of the graph obtained by the least-squares method.
S8. IPCE of Au-Ag alloy NPs and Au NPs on TiO₂ substrates

Figure S7. IPCE action spectra of Au-Ag alloy NP/TiO₂/ITO (red) and Au NP/TiO₂/ITO structures (black) with TiO₂ thicknesses of 21 nm and 28 nm, respectively. The Au-Ag alloy NP and Au NP inlay depth was 7 nm.
S9. Near-field spectra of AATA and ATA

To compare the near-field enhancements of AATA and ATA, finite-difference time-domain (FDTD) simulations were performed to calculate the near-field spectra of AATA and ATA, as shown in Figure S8. The complex refractive index of alloy NPs takes the form

\[
n_{\text{Alloy}} = \frac{7n_{\text{Au}} + 3n_{\text{Ag}}}{10}, \quad k_{\text{Alloy}} = \frac{7k_{\text{Au}} + 3k_{\text{Ag}}}{10}
\]

where \(n_{\text{Au}}\) and \(n_{\text{Ag}}\) are the refractive indices of Au and Ag, and \(k_{\text{Au}}\) and \(k_{\text{Ag}}\) are the extinction coefficients of Au and Ag, respectively.\[^{3,4}\]

The complex refractive indices of a Au NP and TiO\(_2\) from Ciesielski et al\[^{3}\] and Sarkar et al\[^{5}\] were used, respectively. The surrounding medium of the model structure was set to be water. The FDTD monitor was placed at the interface between the metal NP and TiO\(_2\).

Figure S8. Near-field spectra calculated by the FDTD simulation. (a) Configuration of the FDTD simulation. (b) Near-field spectra of Au-Ag alloy NPs/TiO\(_2\) and Au NPs/TiO\(_2\) with TiO\(_2\) thicknesses of 21 nm and 28 nm, respectively. (c) Near-field spectra of AATA and ATA structures with TiO\(_2\) thicknesses of 21 nm and 28 nm, respectively. The Au-Ag alloy NP and Au NP inlay depth was 7 nm. The diameters of the Au-Ag alloy NP and Au NP were 21 nm and 12 nm, respectively.
S10. References

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S11. Author Contributions

Hiroaki Misawa contributed on the funding acquisition (lead), project administration (lead), validation (equal) formal analysis (equal), and writing the original draft (equal).

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