

Supporting information

Fabrication of a stable Au/Ta₂O₅ plasmonic photoanode for water splitting working under visible light irradiation

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Table of Contents

Experimental (Impedance measurement)

Supplementary Figures

Figure S1. Mott–Schottky plots based on impedance measurements. Plot for (a) Ta₂O₅/FTO and (b) Au/Ta₂O₅/FTO at frequency of 35 kHz.

Figure S2. The effect of the amount of Au modified on Ta₂O₅ on the amount of photocurrent at 0.8 V vs. RHE under irradiation of visible light from a Xe lamp equipped with an L42 cut-filter. All Au/Ta₂O₅/FTO electrodes were prepared under the same conditions (described in experimental section).

Figure S3. Time courses of the amounts of H₂ and O₂ from water over Au/Ta₂O₅/FTO at 0.8, 1.0, and 1.2 V vs. RHE under light irradiation.

Figure S4. (a) Au L_{III}-edge XANES spectra of Au/Ta₂O₅/FTO before and after the photoelectrochemical measurements and (b) XPS spectra around the Au 4f component.

Figure S5. Photoabsorption spectrum and IPCE action spectrum of the Au/Ta₂O₅/FTO photoelectrode.

Table S1 Summary of several reported results for water splitting and water oxidation using photoanodes.

Supporting information

Experimental (Impedance measurement)

Impedance measurements were done in a three-electrode electrochemical cell using Ta₂O₅/FTO or Au/Ta₂O₅/FTO, Ag/AgCl, and Pt wire as the working electrode, reference electrode, and counter electrode, respectively. An aqueous Na₂SO₄ solution (0.1 M, pH 6) was used as an electrolyte. Before the measurements, the dissolved air was removed by purging with Ar gas for 30 min. The imaginary component of the impedance (Z'') of the equivalent circuit including the Ta₂O₅/FTO or Au/Ta₂O₅/FTO electrodes were evaluated at three current frequencies of 35 kHz with sweeping applied voltage from -0.85 to 0.75 V vs. Ag/AgCl using an electrochemical measurement system (HZ-7000, Hokuto Denko, Hyogo).

Flatband potential values from impedance measurements were obtained from the extrapolation of Mott-Schottky plots (C^{-2} vs. applied potential) using the following equation (S1):

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 A e N_D} \left(E - E_{FB} - \frac{k_B T}{e} \right) \quad (S1)$$

where C is the space capacitance (calculated from equation (S2)), ε is the dielectric constant of the semiconductor, ε_0 is the permittivity of free space, A is the interfacial area, N_D is the number of donors, E is the externally applied potential, E_{FB} is the flatband potential at the semiconductor/electrolyte junction, k_B is Boltzmann's constant, T is the absolute temperature, and e is the electronic charge,

$$|Z''| = \frac{1}{2\pi f C} \quad (S2)$$

The difference in the potential (E) derived from the pH value of the electrolyte solution was revised in accordance with the Nernst equation (S3):

$$E(\text{pH} = a) = E(\text{pH} = b) - 0.059 \times (a - b) \quad (S3)$$

The potential (vs. Ag/AgCl) was converted to the potential (vs. NHE) by the following equation (S4):

$$E(\text{vs. NHE}) - E(\text{vs. Ag/AgCl}) = 0.199 \text{ V} \quad (S4)$$

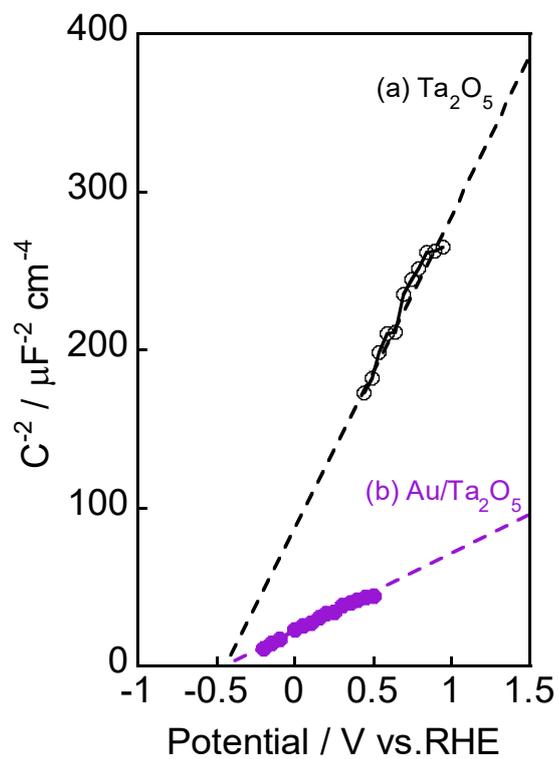


Figure S1. Mott-Schottky plots based on impedance measurements. Plot for (a) $\text{Ta}_2\text{O}_5/\text{FTO}$ and (b) $\text{Au}/\text{Ta}_2\text{O}_5/\text{FTO}$ at frequency of 35 kHz.

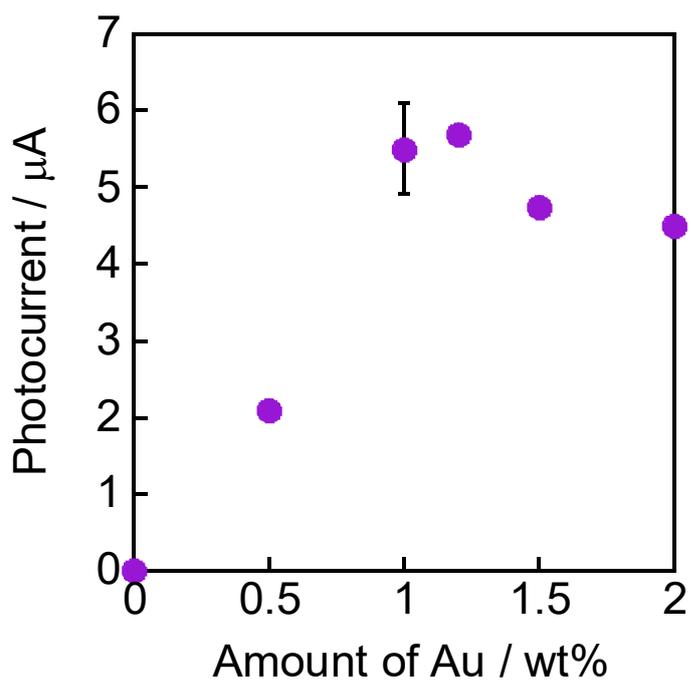


Figure S2. The effect of the amount of Au modified on Ta₂O₅ on the amount of photocurrent at 0.8 V vs. RHE under irradiation of visible light from a Xe lamp equipped with an L42 cut-filter. All Au/Ta₂O₅/FTO electrodes were prepared under the same conditions (described in experimental section).

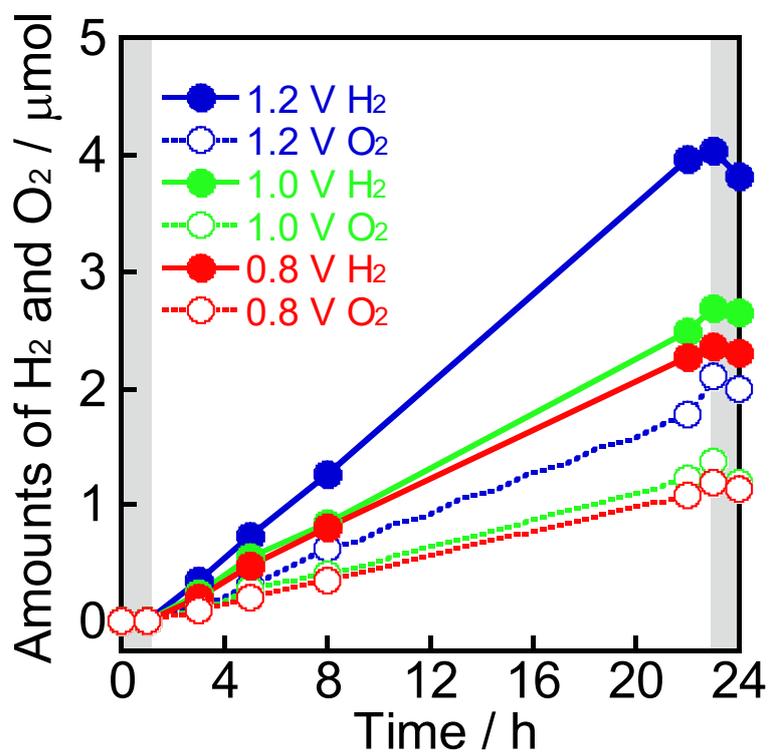


Figure S3. Time courses of the amounts of H₂ and O₂ from water over Au/Ta₂O₅/FTO at 0.8, 1.0, and 1.2 V vs. RHE under light irradiation. Visible light from a Xe lamp equipped with an L42 cut filter was irradiated to the electrodes.

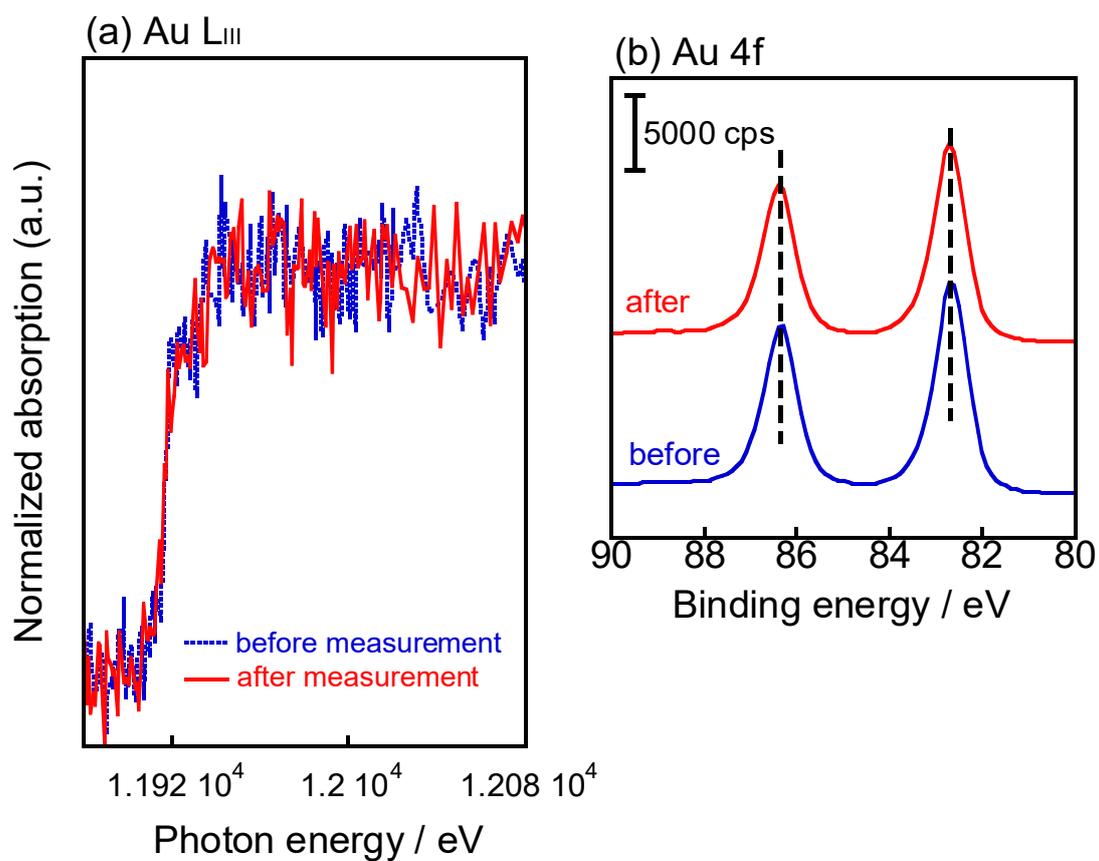


Figure S4. (a) Au L_{III}-edge XANES spectra of Au/Ta₂O₅/FTO before and after the photoelectrochemical measurements and (b) XPS spectra around the Au 4f component.

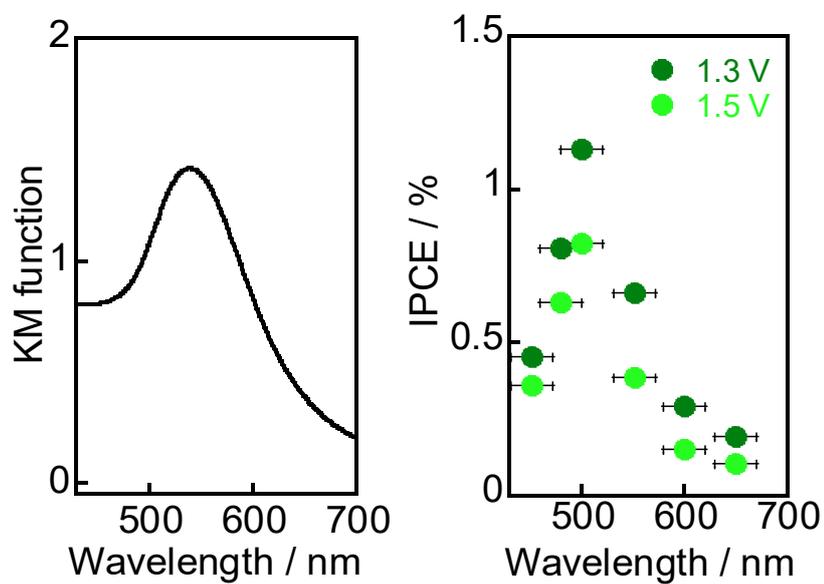


Figure S5. Photoabsorption spectrum and IPCE action spectrum of the Au/Ta₂O₅/FTO photoelectrode. The IPCE measurement was conducted at +1.3 V and + 1.5 V vs. RHE.

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Table S1 Summary of several reported results for water splitting and water oxidation using photoanodes.

Entry	electrode	type	reaction	light	activity	Faraday efficiency	IPCE	DOI
This study	Au/Ta ₂ O ₅	sensitization	water splitting	Xe lamp (L42)	H ₂ : 101 nmol h ⁻¹ ; O ₂ : 52 nmol h ⁻¹ 0.8 V vs. RHE	65 %	0.6 % (0.7 V vs. RHE, 420 nm)	-
1	Ni(OH) ₂ /Au NP/TiO ₂	sensitization	water splitting	Xe lamp (460 nm long-pass filter)	H ₂ : 190 nmol h ⁻¹ ; O ₂ : 75 nmol h ⁻¹ 0.2 V vs. Ag/AgCl	n/a	ca. 0.1 % (0.2 V vs. Ag/AgCl, 600 nm)	10.1002/cnma.201900187
2	CoO _x /Au/TiO ₂	sensitization	water oxidation	solar simulator	O ₂ : 2 μmol h ⁻¹ 0.66 V vs. RHE	n/a	0.8 % (0.9 V vs. RHE, 600 nm)	10.1021/acsaem.0c00857
3	Co/TiO ₂	sensitization	water oxidation	Xe lamp (Y44)	O ₂ : 70 nmol h ⁻¹ 0.56 V vs. RHE	12 %	0.9 % (0.56 V vs. RHE, 500 nm)	10.1021/acsami.9b20793
4	Ru dye(RuP1)/TiO ₂	sensitization	water oxidation	Xe lamp (400 nm long-pass filter)	O ₂ : 142 nmol h ⁻¹ 0 V vs. Pt	74 %	1.85 % (0 V vs. Pt, 455 nm)	10.1016/j.electacta.2014.10.111
5	TiO ₂ -coated Au nanodots	sensitization	water splitting	Dolan Jenner fiber-optic light	H ₂ : 7 μmol h ⁻¹ ; O ₂ : 4 μmol h ⁻¹ 0.897 V vs. SHE	94.9 %	n/a	10.1021/nn504484u
6	CoO _x /TaON	bandgap	water splitting	Xe lamp (L42)	H ₂ : 134 μmol h ⁻¹ ; O ₂ : 67 μmol h ⁻¹ 1.07 V vs. RHE	n/a	42 % (1.2 V vs. RHE, 400 nm)	10.1021/ja302059g
7	Ti/WO ₃ /Mo-BiV	bandgap	water splitting	Blu LED (454 nm)	H ₂ : 60 μmol h ⁻¹ ; O ₂ : 30 μmol h ⁻¹ 1.2 V vs. RHE	94 %	10.7 % (1.2 V vs. RHE, 454 nm)	10.1021/acssuschemeng.0c02331
8	IrO ₂ -TaON	bandgap	water splitting	Xe lamp (L42)	H ₂ : 26 μmol h ⁻¹ ; O ₂ : 12 μmol h ⁻¹ 1.0 V vs. Pt	n/a	76 % (0.6 V vs. Ag/AgCl, 400 nm)	10.1021/ja1016552
9	w-α-Fe ₂ O ₃	bandgap	water oxidation	Xe lamp (L42)	O ₂ : 3 μmol h ⁻¹ 1.23 V vs. RHE	ca. 100 %	13 % (1.23 V vs. RHE, 420 nm)	10.1021/acsami.1c08949
10	CdS	bandgap	CO ₂ reduction	Xe lamp (L42)	CO: 20 μmol h ⁻¹ 0.5 V vs. Ag	n/a	n/a	10.1039/d1nj06073b
11	WO ₃	bandgap	HClO production	AM 1.5G	HClO: 1.76 μmol h ⁻¹	96 %	0.9% (-, 420 nm)	10.1021/acssuschemeng.0c01341