Supplemental Information

Active Intermediates in Plasmon-Induced Water Oxidation at Au Nanodimer Structures on a Single Crystal of TiO₂

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Methods and Preparation

Materials

The chemicals used in this work were of ultra-high purity:

Hydrofluoric acid (HF, \geq 40%, Sigma-Aldrich), perchloric acid (HClO₄, 60%, Wako), potassium hydroxide (KOH, 99.99%, Sigma-Aldrich), deuterium oxide (D₂O, 99.8%, Wako), water-¹⁸O (H₂¹⁸O, 97 atom % ¹⁸O, Sigma-Aldrich), super-pure reagents and Milli-Q water (18 MΩ⁻¹ cm⁻¹) water was used for all the experiments in this work.

Preparation of triangular Au nanodimers

All glassware was rigorously cleaned before starting experiments by boiling in concentrated H₂SO₄ to remove metals and organic contaminants and was subsequently boiled twice in Milli-Q water, which was also used to prepare the solutions for the electrochemical experiments.

TiO₂ single crystalline (rutile, 0.05 wt % niobium doped, $10 \times 10 \times 0.5 \text{ mm}^3$, Furuuchi Chemical Corporation) with a (110) facet was used as a photoelectrode. The TiO₂ substrate was first rinsed with acetone and Milli-Q water in an ultrasonic bath for 10 min, then immersed into a 20% HF solution for 10 min, followed by rinsing, drying in nitrogen flow, and annealing at 600°C for 150 min. The hydrophilic TiO₂ surface was obtained by treatment under ultraviolet irradiation for 30 min. Size-controlled Au triangular nanodimer arrays presenting localized surface plasmon resonance (LSPR) were fabricated on a TiO₂ single crystalline (noted as Au/TiO₂) or indium tin oxide (noted as Au/ITO) by angle-resolved nanosphere lithography (AR-NSL) using polystyrene microspheres (PS beads, Polybead® polystyrene microspheres, diameter = 200 nm, Polysciences, Inc.) with an average diameter of 200 nm. Details can be found in our previous works. Au nanostructures fabricated by this method show high SERS activity, especially at the gap between a Au triangular nanodimer.¹⁻³

Morphology characterization

The morphology of the electrode was measured by a field-emission scanning electron microscope (FE-SEM, JSM-6700FT) using a 5.0-kV electron beam with various magnifications.

EC-SERS measurement

In-situ Surface Enhanced Raman Spectroscopy (SERS) was performed with a homemade polarized Raman microscope (FN2M–SP, PHOTON Design) with a ×100 water-immersion objective (N.A. = 1.0, Olympus). The excitation source used was a NIR laser light of 785 nm ($E_{ex} = 1.58 \text{ eV}$) (Xtra-PS 00369, TOPTICA Photonics). The output laser intensity was tuned via a ND filter yielding an estimated spot size of irradiation of ~1 µm and intensity of 1 mW, as measured via power meter (OPHIR Japan LTD.). Raman measurements were carried out at the scattering configuration, collecting the scattering photons at the backscattering configuration (the laser beam and scattered light perpendicular to the sample plane), and collecting the scattered light was filtered with an edge filter at 985 nm, subsequently directed to the spectrograph and to the CCD detector (PIXIS 256, Princeton Instruments). Further details of the setup can be found in our previous work.⁴ EC-SERS measurements were carried out via a three-electrode system in the following electrolytes: 1.0 M HClO₄ pH 0, 0.1 M NaF pH 7, and 0.1 M KOH pH 13. A handmade Ag/AgCl (sat. KCl) was used as a

reference electrode. (All potentials in this work are reported *vs*. this reference electrode unless otherwise stated.). A platinum narrow plate was used as a counter electrode, and Au/TiO₂ or Au/ITO was the working electrode; the reference electrode was separated from the working electrode compartment to avoid chloride contamination (Figure 1d). For the Au/TiO₂ electrode, an indium–gallium alloy film was pasted on the back of the TiO₂ substrate and connected to the potentiostat with a Pt wire for ohmic contacts. The electrochemical experiments were controlled by a potentiostat (HECS 990C, HosouElectroChemicalSystem) and monitored by an oscilloscope (midi LOGGER GL900, HTEC). SERS spectra for the same sample site were recorded with an acquisition time of 30 s for Au/TiO₂ and 10 s for Au/ITO.

For the Au/TiO₂ electrode, from which strong Raman signals were observed from the pristine TiO₂, obtained SERS spectra at each potential were subtracted with respect to the flat-band potential of the TiO₂ single crystalline (rutile, (110) surface) at each pH value (see details in Results). Thus, the few spectral changes induced from a Au nanostructure can be discussed. The isotopic effect was examined using 99.9 % D₂O and 97 % H₂¹⁸O. Acid, neutral and alkaline conditions were obtained using 1 M HClO₄, 0.1 M NaF and 0.1 M KOH, respectively.

1. Raman spectra of bare TiO₂ and differential spectra



Figure S1. (Left) Raman spectra of bare rutile TiO₂ single crystallite under perpendicular (red) and parallel (black) polarization with respect to the direction of the <001> facet of TiO₂. Raman bands appeared at 445 (E_g) and 606 cm⁻¹ (A_{1g}) are assigned to typical rutile phase. The polarization anisotropy is attributed to the enhancement of vibrations corresponding to the direction of optical electric field. Laser wavelength of 785 nm, laser power of 1.00 mW, acquisition for 30 s. (Right) Differential Raman spectra of bare rutile TiO₂ electrode at increasing potential (-0.3, 0, 0.3, and 0.6 V vs Ag/AgCl) in 0.1 M NaF pH 7 electrolyte. The spectrum measured at flat-band potential of -0.57 V was used as the reference spectrum.



2. Measured EC-SERS spectra of Au/TiO₂ electrode

Figure S2. Measured EC–SERS spectra of Au/TiO₂ electrode at different potentials in 0.1 M NaF pH 7 electrolyte (left) and 0.1 M KOH pH 13 electrolyte (right) under longitudinal polarization. Raman spectra recorded at -0.57 V at pH 7 and -0.93 V (both vs. Ag/AgCl) at pH 13 were used for the reference spectrum to obtain the differential spectra for Au/TiO₂ electrode, according to the flat-band potential of single crystal TiO₂ at the corresponding pH electrolytes.

3. Raman bands assignment

Electrode	Assignment		1.0 M HClO ₄ (pH 0)			0.1 M NaF (pH 7)			0.1 M KOH (pH 13)		
	Mode	Intermediate	Raman shift	Ag/AgCl	RHE ^a	Raman shift	Ag/AgCl	RHE	Raman shift	Ag/AgCl	RHE
Au/TiO ₂	v(Au–O)	b	564, b ^c	-0.2	0.00	572	-0.5	0.11	545	-1.0	-0.03
Au/ITO	v(Au –	Au2*(OH)4	470, w, sh	1.3	1.50	460, w, sh	0.6	1.21	440-500, w, sh	0.3	1.27
	OH)										
	v(Au–O)	Au(OH) ₃	550–580, b	1.3	1.50	550-565, shp	0.6	1.21	550-570, shp	0.4	1.37
		AuOOH	600, shp	1.5	1.70	580, b	1.3	1.91	580, b	0.7	1.67
		Au_2O_3	650-720, sh	1.5	1.70	650–700, sh	1.2	1.81	650–680, sh	0.6	1.57
	ν(O–O)	AuOOH	800, w	1.6	1.80	810, vw	1.3	1.91	800, vw	0.9	1.87

Table S1 Raman shift (cm⁻¹) for Au hydroxide intermediates and the corresponding potentials (V).

^a $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 \times \text{pH} + E^{\circ}_{\text{Ag/AgCl}}$, where $E^{\circ}_{\text{Ag/AgCl}} = 0.199 \text{ V}$

^b AuOOH at pH 7; Au(OH)₃ at pH 0 and 13 (see the text for details).

^c Relative intensity: b, broad; v, very; w, weak; s, strong; sh, shoulder; shp, sharp.

4. Isotope effect

		0.1 M		4 (H ₂ O vs	s. D ₂ O)	0.	1 M NaF (p	H 7) (H ₂ ¹⁶	O vs. H ₂ ¹⁸ O)
	Au/ŤiO ₂	3 cps	' Au/	τd ' '	25 cps	Au/TiO ₂	4 cps	Au/ITO	30 cps
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Figure S3. The isotope effect in Raman shift of Au–O stretching mode on Au/TiO₂ and Au/ITO electrode respectively in (left) 0.1 M NaClO₄ prepared with D₂O (blue line) and H₂O water (black line) and (right) 0.1 M NaF prepared with H₂¹⁸O (orange line) and H₂¹⁶O water (black line) . Potential–dependent SERS spectra were acquired by 785 nm laser with laser power of 1.00 mW and acquisition time of 30 s for Au/TiO₂ and 10 s for Au/ITO. Lines present the band maximums.

Raman shift	(cm ⁻¹) &		1 M HClO4		0.1 M	NaClO ₄	0.1 M NaF	
isotopic rela	tive shift	H2 ¹⁶ O	D ₂ ¹⁶ O	H2 ¹⁸ O	$H_2^{16}O$	D2 ¹⁶ O	H ₂ ¹⁶ O	H ₂ ¹⁸ O
	v(Au-O)				570	570	576	545
	v(nu O)					(0 %)		(-5.38 %)
Au/110	w(O_OH)				796	805	796	763
	v(O OII)					(1.13 %)		(-4.15 %)
	(1 0)				576	576	580	536
Au/1102	v(Au-O)					(0%)		(-7.59 %)
Describe Ass		589	581	567				
Kougn Au	v(Au-O)		(-1.19 %)	(-3.74 %)				
Surface (1.9 V	v(O-OH)	810	810	734				
vs KHE) ²			(0%)	(-9.38 %)				

Table S2. Assignments of observed Raman modes.

5. Cyclic voltammetry (CV) measurement of Au wire

Current vs. potential curves were obtained with a commercial potentiostat and potential programmer (HSV-110, Hokuto Denko) with a Pt wire as the counter electrode and a Ag/AgCl (sat. KCl) electrode as the reference electrode. The electrolyte solution was prepared using highly pure Milli-Q water and reagent grade chemicals. We used 0.1 M NaF solution in the neutral condition, 1 M HClO₄ in the acid condition, and 0.1 M KOH in the alkaline condition as the electrolyte solution to measure the CV plots under the same conditions as *in-situ* SERS. To measure CV plots under an inert gas atmosphere, argon gas was pumped into the prepared electrolyte solution before the measurements and was kept flowing in a cell during the measurements.



Figure S4 Cyclic voltammetry of Au wire showing "surface oxide" formation, acquired at 50 mV/s in 1.0 M HClO₄ pH 0 electrolyte (blue), 0.1 M NaF pH 7 electrolyte (orange) and 0.1 M KOH pH 13 electrolyte (red), respectively.

6. pH-dependent photocurrent

To further elucidate the plasmon-induced electron-hole separation process for the Au/TiO₂ system, photocurrent was also examined at Au/TiO₂ electrode in 1.0 M HClO₄ pH 0 electrolyte, 0.1 M NaF pH 7 electrolyte and 0.1 M KOH pH 13 electrolyte, respectively. Signals were recorded via steady-state on-off action under visible light irradiation with a wavelength range of 540–800 nm. The three electrolytes used were degassed by nitrogen for 30 min before performing photoelectrochemical measurements controlled from -0.6 V to 0.6 V. Photocurrent signals at potentials negative than 0.1 V in the pH 0 electrolyte and -0.2 V in the pH 7 electrolyte were not observed.



Figure S5. Comparison of recorded photocurrents at 0.6 V vs. RHE in pH 0 (blue), pH 7 (orange) and pH 13 electrolyte (red), respectively.

References

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