

## Electronic Supplementary Information (ESI)

### "Microelectrode-based transient amperometry of O<sub>2</sub> adsorption and desorption on a SrTiO<sub>3</sub> photocatalyst excited under water"

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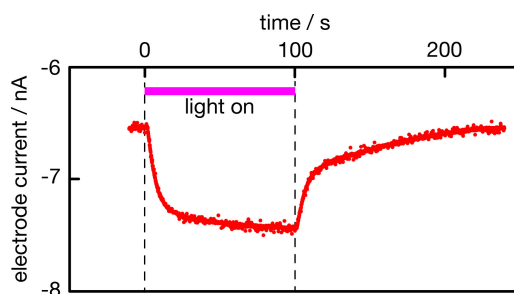
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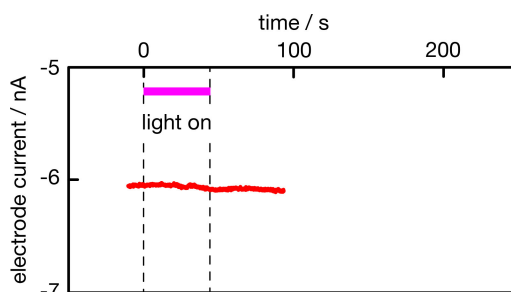
#### S1. Reagents

The reagents used for these experiments included KCl (99.5%, Nacalai tesque), K<sub>2</sub>SO<sub>4</sub> (99.0%, Wako), platinum wire with a 10 μm radius (99.98%, Nilaco), silver wire with a 0.5 mm radius (99.99%, Nilaco), and ultrapure water produced by Direct-Q 3UV (Millipore).

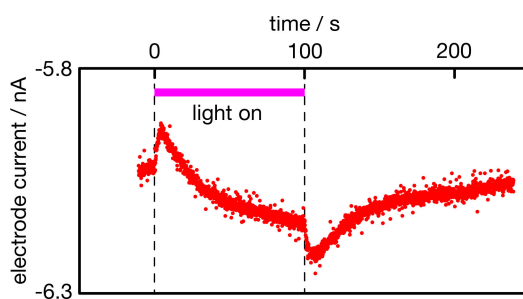
## S2. Experimentally observed current responses



**Fig. S1** Current response on a photocatalyst film just immersed in the KCl solution. The film was immersed in the solution for 4 h without being modified by intense ( $30 \text{ W m}^{-2}$ ) light irradiation. Light for probing was irradiated on the modified film at  $t = 0\text{--}100.4 \text{ s}$ . The distance between the electrode and film  $d$  was  $100 \mu\text{m}$ .



**Fig. S2** Current response without the photocatalyst film. A Pt microelectrode was immersed in the KCl solution and irradiated with intense ( $30 \text{ W m}^{-2}$ ) light for 4 h. The current response was then immediately observed in the absence of the photocatalyst film. Light for probing ( $3 \text{ W m}^{-2}$ ) was irradiated at  $t = 0\text{--}43.8 \text{ s}$ .



**Fig. S3** Current response in a  $\text{K}_2\text{SO}_4$  solution. The photocatalyst film was irradiated with intense ( $30 \text{ W m}^{-2}$ ) light for 4 h in an aqueous  $\text{K}_2\text{SO}_4$  solution ( $0.1 \text{ mol l}^{-1}$ ). The irradiated film was immediately probed in the same solution. Light for probing ( $3 \text{ W m}^{-2}$ ) was irradiated at  $t = 0\text{--}99.9 \text{ s}$ . The electrode–film distance,  $d$ , was  $100 \mu\text{m}$ .

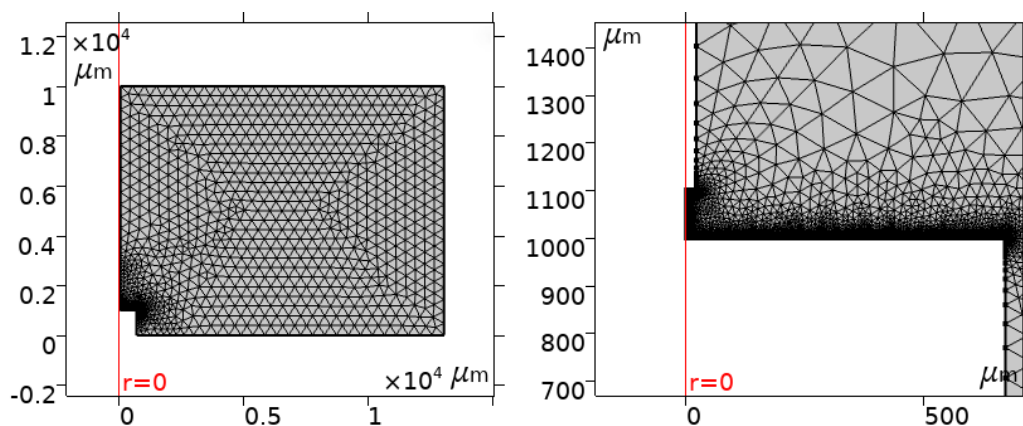
### S3. Simulation details

The photocatalytically produced  $O_2$  was released on the film surface, diffused in the solution, and finally collected on the electrode. Diffusion in the solution was driven by a concentration gradient, as described by Fick's second law. Finite-element integration in cylindrical space, which was defined in Fig. 2(A) of the main text, was conducted using COMSOL Multiphysics v. 5.4. Although the microelectrode blocked the UV light, the shadow on the photocatalyst film was not considered in the simulations. The electrode–film distance was in the range of 100–200  $\mu\text{m}$ , while the diameter of the electrode making shadows was estimated to be 40  $\mu\text{m}$ . The film beneath the electrode was not shadowed.

**S3.1. Object size and finite element meshes.** All object dimensions other than the photocatalyst film radius,  $R_{photo}$ , were set to experimentally determined lengths.

- Platinum electrode section radius,  $a$ : 10  $\mu\text{m}$
- Glass wrap radius,  $R_g$ : 20  $\mu\text{m}$
- Electrode–film distance,  $d$ : experimentally determined distance (100, 150, or 200  $\mu\text{m}$ )
- Photocatalyst plate thickness,  $Z_{photo}$ : 1 mm
- Solution vessel radius,  $R_{solution}$ : 13 mm
- Solution thickness,  $Z_{solution}$ : 10 mm

The radius of the irradiated photocatalyst film,  $R_{photo}$ , was tuned to fit the observed current response.  $R_{photo}$  was difficult to quantitatively determine. The spot spread on the film had a graded boundary. The meshes used to define the elements for integration are illustrated in Fig. S4.



**Fig. S4** Meshes for integration in (left) complete and (right) partial view.

**S3.2. Boundary conditions.** Assuming that the background concentration had equilibrated with the air, we can describe the change in oxygen concentration,  $C_{\text{change}}$ , relative to the background concentration using Fick's law:

$$\frac{\partial C_{\text{change}}}{\partial t} = D \left( \frac{\partial^2 C_{\text{change}}}{\partial t^2} + \frac{1}{r} \frac{\partial C_{\text{change}}}{\partial r} + \frac{\partial^2 C_{\text{change}}}{\partial z^2} \right).$$

The equation was integrated to determine  $C_{\text{change}}$  on the meshes shown in Fig. S4 with time steps of 0.1 s using the following conditions:

- $C_{\text{change}}$  was zero everywhere in the solution at  $t = 0$ .
- $C_{\text{change}}$  was always zero at the solution surface facing the air.
- $C_{\text{change}}$  was always zero at the electrode–solution interface since the four-electron reduction quickly consumed  $\text{O}_2$ , i.e., the electrode current was limited by  $\text{O}_2$  diffusion.

The  $\text{O}_2$  release rate on the film resulted in a vertical gradient of  $C_{\text{change}}$  at the film–solution interface:

$$D \left( \frac{\partial C_{\text{change}}}{\partial z} \right) = \text{O}_2 \text{ release rate.}$$

The other solid–solution interfaces produced or consumed no oxygen:

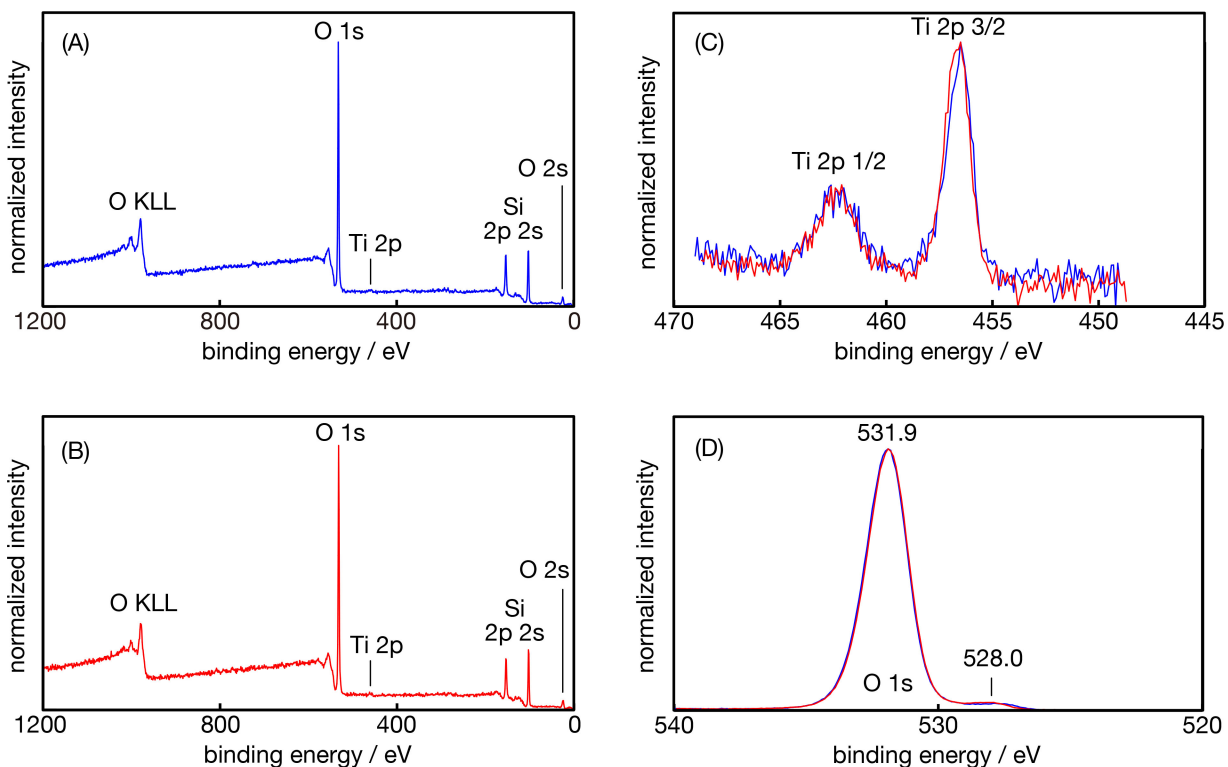
$$\frac{\partial C_{\text{change}}}{\partial r} = \frac{\partial C_{\text{change}}}{\partial z} = 0.$$

**S3.3. Electrode current change.** Electrode current change,  $\Delta I$ , was predicted by the following integration at the  $t$  value of interest:

$$\Delta I = 4F \times 2\pi \int_0^a D \left( \frac{\partial C_{\text{change}}}{\partial z} \right)_{z=d} r dr.$$

#### S4. Film characterization using X-ray photoelectron spectroscopy

A photocatalyst film was modified by intense light irradiation ( $30 \text{ W m}^{-2}$  for 4 h) of the KCl solution. The surface composition of the original and modified films was analyzed with X-ray photoelectron spectroscopy using a spectrometer (Ulvac-Phi, X-tool) with an Al  $K\alpha$  excitation source. The wide-scan spectra indicated major signals for oxygen, silicon, and titanium. Strontium emissions were present but not visible in the spectra shown in Fig. S5. No other element was detected. The presence of Si was expected since the  $\text{SrTiO}_3$  particles were casted with  $\text{SiO}_2$  particles on a glass plate. Titanium 2p emissions were further checked to examine the valence state of the Ti cations. The twin peaks (2p  $3/2$  and 2p  $1/2$ ) remained intact during intense light irradiation, as shown in (C), with no sign of reduction from the 4+ to 3+ state. Two O 1s peaks appeared at 531.9 and 528.0 eV in (D), which were attributed to oxygen anions in  $\text{SiO}_2$  and  $\text{SrTiO}_3$ , respectively. The shape and intensity of the two O 1s peaks were not perturbed by intense light irradiation.

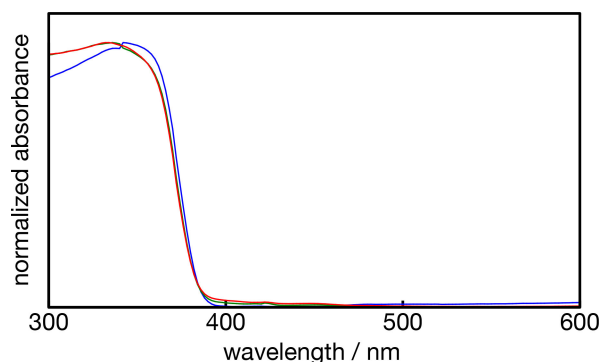


**Fig. S5** X-ray photoelectron spectra of the photocatalyst film before (blue) and after (red) intense light irradiation ( $30 \text{ W m}^{-2}$  for 4 h) in the KCl solution. Intensity was normalized at the maximum in each spectrum. (A) and (B): wide-scan spectra of the original and modified films. (C) and (D): narrow-scan spectra of Ti 2p and O 1s emissions. The binding energy of the red spectra in (C) and (D) was shifted by  $-0.1$  to  $-0.3$  eV relative to that of the blue spectra in order to compensate for possible energy shifts during charging. The photocatalyst films were electrically isolated on the glass plate and hence were possibly affected by charging under X-ray irradiation in the vacuum.

### S5. Film characterization with optical absorption

Optical absorption of the pristine and modified films was examined in the wavelength range of 300–600 nm. Fig. S6 presents the diffuse-reflection spectra determined using a spectrometer (Jasco, V-570) with an integration sphere. The pristine dried film followed the blue spectrum with an absorption edge at 370 nm, which was defined by the wavelength corresponding to half of the maximum absorbance, being consistent to a previous report.<sup>S1</sup> The film was immersed in the KCl solution for 4 h with no light irradiation, removed from the solution, and immediately installed in the integration sphere. The green spectrum observed on the moist film showed that the absorption edge blue-shifted by 2 nm. In addition, weak absorption was recognized in the range of 390–470 nm. These minor changes may have resulted from different light-scattering properties of solid particles in the dry and moist films. The film was irradiated with intense light

for 4 h in the KCl solution on another day and immediately installed in the sphere. The observed spectrum (red curve) was identical to the green spectrum. Thus, the film showed no sign of absorption change induced by the light irradiation.



**Fig. S6.** Optical absorption of a photocatalyst film. The blue curve shows the spectrum observed on the dried film prior to immersion in the KCl solution. The green spectrum presents absorption of the film immersed in the solution for 4 h without light irradiation. The red curve depicts the spectrum of the film immersed in the solution for 4 h under intense light irradiation ( $30 \text{ W m}^{-2}$ ). The latter two spectra were observed on the moist films. The raw absorbance was normalized at the maximum of each spectrum and shown without Kubelka–Munk transformation.

## Reference

- (S1) Y. Ham, T. Hisatomi, Y. Goto, Y. Moriya, Y. Sakata, A. Yamakata, J. Kubota and K. Domen, Flux-mediated doping of  $\text{SrTiO}_3$  photocatalysts for efficient overall water splitting. *Mater. Chem. A* 2016, **4**, 3027–3033 and its Supporting Information.