Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Faradaic Oxygen Evolution from $SrTiO_3$ Under Nano- and Femto-Second Pulsed Excitation

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Cyclic voltammetry curve under Xe lamp excitation

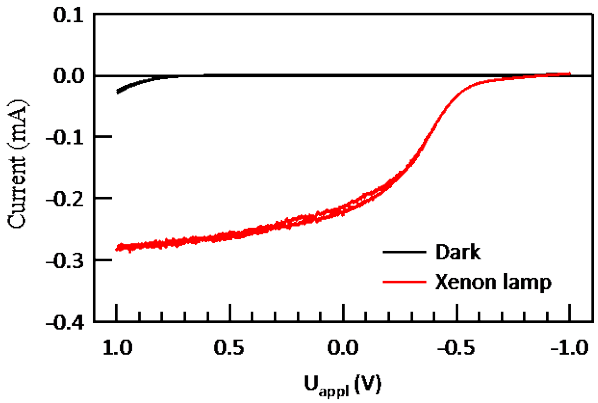

Fig. S 1: Cyclic voltammogram of n-$SrTiO_3$ in the dark and under irradiation by a 150 W Xenon lamp. Similar to the current-voltage curve under laser irradiation (Figure 1a of the main text), a diode-like behavior was observed under Xenon lamp irradiation.

Laser spot size determination

The spot size of the laser is determined by knife edge scan. Pulsed laser beam can be treated approximately as a Gaussian beam. A sharp knife edge is used and move in very small steps across the laser beam in either horizontal or vertical manner (horizontal as x, vertical as y). For horizontal direction, a laser diode constantly measures the power of laser beam as the knife edge is moving across the laser beam, such that a laser power versus knife edge position profile can be obtained. Then the intensity versus position profile is fitted with a sigmoid function. The derivative of the sigmoid function is then fitted with a Gaussian function.

$$I\ (x) = I_0 \frac{1}{\sigma\sqrt{2\pi}} e^{\frac{-x^2}{2\sigma^2}}\ (Equation\ S1)$$

Such that the standard deviation σ can be extracted and the full width half maximum can be calculated by

$$w(x) = 2\sqrt{2\ln(2)}\sigma\ (Equation\ S2)$$

The same procedure applied to vertical (y) direction of the beam and $w(y)$ can be obtained. Then the laser spot size is calculated by

$$Spot\ size = \ \pi \times \frac{w(x)}{2} \times \frac{w(y)}{2}\ (Equation\ S3)$$

ICP calculation of photodissolution on n-$SrTiO_3$ photoelectrode

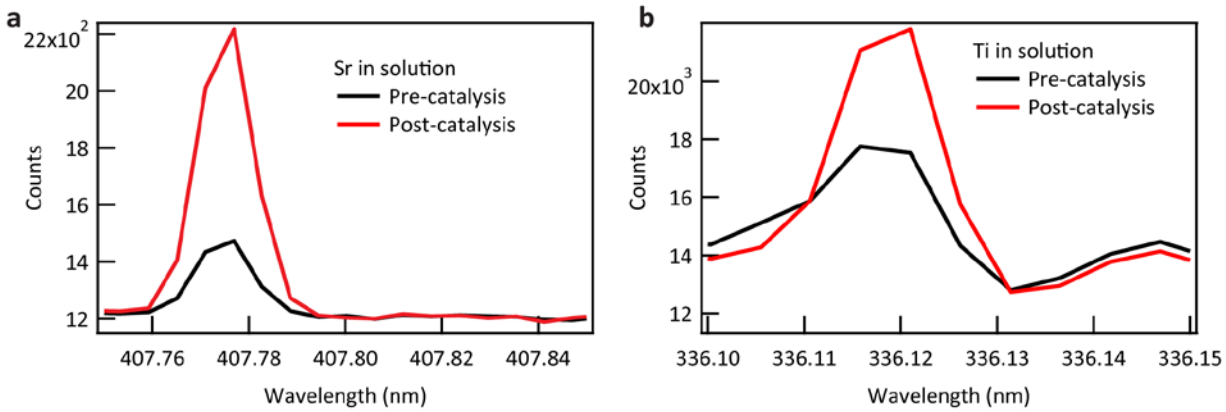

Fig. S 2: ICP spectra of a) Sr metal in solution and b) Ti metal in solution pre- and post-catalysis

ICP analysis is also performed to examine photodissolution during catalysis. Fig. S 2A shows the Sr concentration in solution increasing after catalysis taken place. Fig. S 2B shows the same is happening to Ti. Quantitatively, according to the calibration curve for Sr and Ti, the concentration for both species is 5 ppb which corresponds to a molar concentration of 1.71×10^{-8} M for both species. Totally 10 ml of solution is used, which gives a total of $1.71 \times 10^{-10}\ mol$ Sr and Ti in solution. To electrochemically dissolve one mole Sr, 2 moles of electrons are needed as Sr has the form of Sr^{2+} in $SrTiO_3$ crystal. Then, total number of charges to needed to dissolve Sr will be $1.71 \times 10^{-10} mol \times 2 \times N_A \times 1.6 \times 10^{-19} C = 3.3 \times 10^{-5} C$. Typical day of experiments transfer total of 0.182 C of charge, therefore, the efficiency for photodissolution of Sr is $\frac{3.3\times10^{-5}C}{0.182C} \times 100\% = 0.018\%$. Same procedure is applied to Ti and Ti has the form of Ti^{4+}. So the efficiency for photodissolution of Ti is $\frac{6.6\times10^{-5}C}{0.182C} \times 100\% = 0.036\%$. Total efficiency for electrochemical photodissolution is then $0.018\% + 0.036\% = 0.054\%$.

Photocurrent density calculation from transient photocurrent

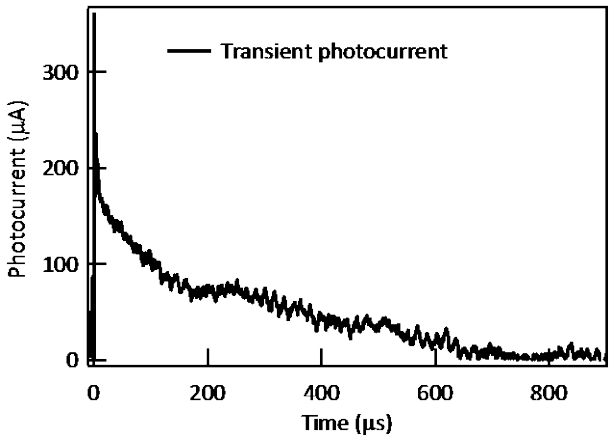

Fig. S 3: Example transient photocurrent under pulsed laser excitation

Transient photocurrent is performed to determine the photocurrent density under pulsed laser condition. Fig. S 3 shows transient photocurrent with 0.05 mJ/cm^2 laser excitation. Integrate the transient photocurrent gives a total of $4.25 \times 10^{-5}\ mC$ of charge generated per laser pulse. The laser repetition rate is 500 Hz, such that for 1s, the total number of charge generated is $4.25 \times 10^{-5}\ mC \times 500 = 2.13 \times 10^{-2}\ mC$. Then the average current density per second can be determined from $\frac{Total\ number\ of\ charge\ per\ second}{laser\ spot\ size} = \frac{2.13 \times 10^{-2}\ mC}{0.0075\ cm^2} = 2.8\ mA\ cm^{-2}$