Supporting Information (13 pages)

Facets Control Charge Separation during Photoelectrochemical Water Oxidation with Strontium Titanate ($SrTiO_3$) Single Crystals

Samutr Assavachin, Chengcan Xiao, Kathleen Becker, and Frank E. Osterloh*

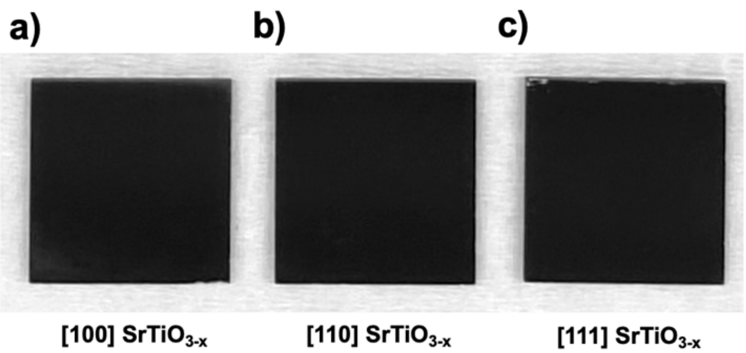

Figure S1. Photos of hydrogen-annealed $SrTiO_{3-x}$ single crystals with a) (100), b) (110), and c) (111) facets. Crystals are 1.0 x 1.0 cm^2 large.

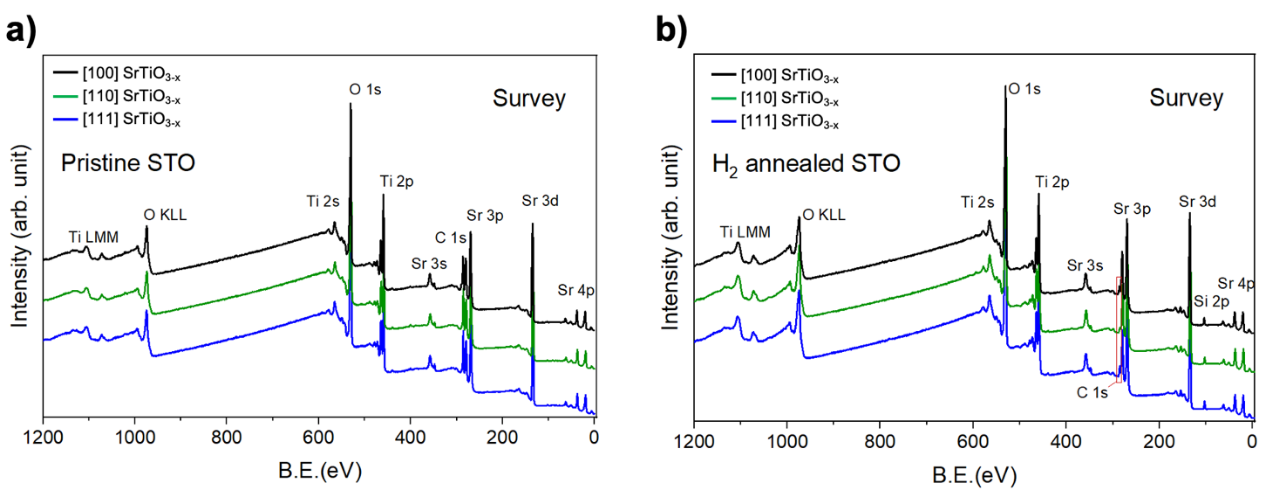

Figure S2. Survey scans of (100), (110), and (111) facets of the $SrTiO_3$ single crystals before (a) and after (b) H_2 annealing. A small Si 2p impurity peak at 102 eV is attributed to migration of Si species from the ceramic crucible used for the H_2 annealing at 1100°C.

Table S1. XPS summary for $SrTiO_3$ single crystals before and after H_2 annealing.

O 1s	Lattice O			Sr-OH			Ti-OH			
	Position	Area	% area	Position	Area	% area	Position	Area	% area	
(100) $SrTiO_3$	529.08	28455.580	73.4	530.18	1069.289	2.8	531.38	9233.749	23.8	
(100) $SrTiO_{3-x}$	529.28	35511.050	58.4	530.38	8926.351	14.7	531.98	16413.640	27.0	
(110) $SrTiO_3$	529.02	23034.040	66.3	530.02	742.980	2.1	531.12	10969.540	31.6	
(110) $SrTiO_{3-x}$	529.24	37989.690	61.6	530.34	9944.254	16.1	531.94	13737.490	22.3	
(111) $SrTiO_3$	528.90	25127.190	70.9	530.00	3591.105	10.1	531.3	6719.895	19.0	
(111) $SrTiO_{3-x}$	529.34	34271.930	56.3	530.34	9944.254	19.8	531.94	14569.490	23.9	
Ti 2p	Ti^{4+} $2p_{3/2}$			Ti^{4+} $2p_{1/2}$		Ti^{3+} $2p_{3/2}$			Ti^{3+} $2p_{1/2}$	
	Position	Area	% area	Position	Area	Position	Area	% area	Position	Area
(100) $SrTiO_3$	457.98	18701.270	-	463.68	9350.637	-	-	-	-	-
(100) $SrTiO_{3-x}$	458.18	25095.470	89.2	463.98	12547.730	456.28	3053.007	10.8	462.18	1526.504
(110) $SrTiO_3$	457.92	18364.61	-	463.62	9182.303	-	-	-	-	-
(110) $SrTiO_{3-x}$	458.24	29828.030	91.0	464.04	14914.020	456.14	2958.796	9.0	462.24	1479.398
(111) $SrTiO_3$	457.80	18670.750	-	463.60	9335.377	-	-	-	-	-
(111) $SrTiO_{3-x}$	458.34	28265.560	91.7	464.04	14132.780	456.24	2565.564	8.3	462.24	1282.782
Sr 3d	Sr $3d_{5/2}$			Sr $3d_{3/2}$		Surface Sr $3d_{5/2}$			Surface Sr $3d_{3/2}$	
	Position	Area	% area	Position	Area	Position	Area	% area	Position	Area
(100) $SrTiO_3$	132.48	20854.110	-	134.28	13902.81	-	-	-	-	-
(100) $SrTiO_{3-x}$	132.58	21262.600	71.7	134.38	14175.140	133.28	8371.931	28.3	134.98	5581.315
(110) $SrTiO_3$	132.48	19748.21	-	134.12	13165.48	-	-	-	-	-
(110) $SrTiO_{3-x}$	132.74	26611.890	80.9	134.44	17741.350	133.44	6275.025	19.1	135.14	4183.37
(111) $SrTiO_3$	132.40	18647.890	-	134.10	12431.990	-	-	-	-	-
(111) $SrTiO_{3-x}$	132.74	22134.040	78.2	134.54	14756.100	133.54	6187.937	21.8	135.24	4125.312

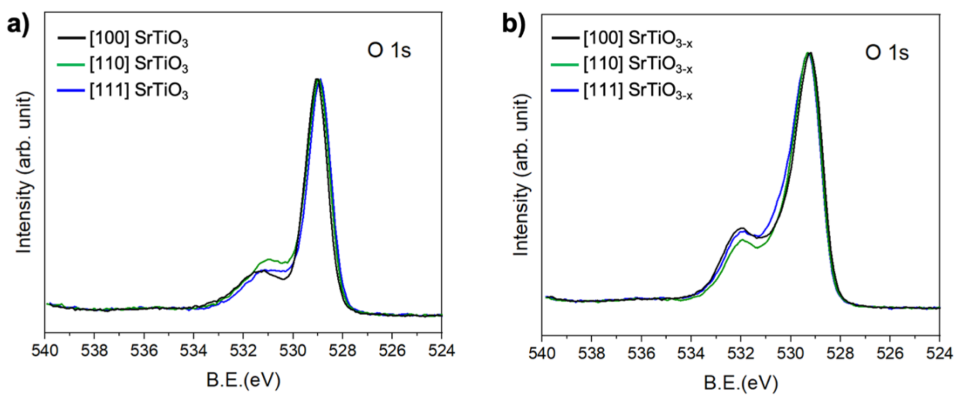

Figure S3. Overlapped high resolution O1s region for (100), (110), and (111) facets of $SrTiO_3$ single crystal a) before and b) after H_2 annealing.

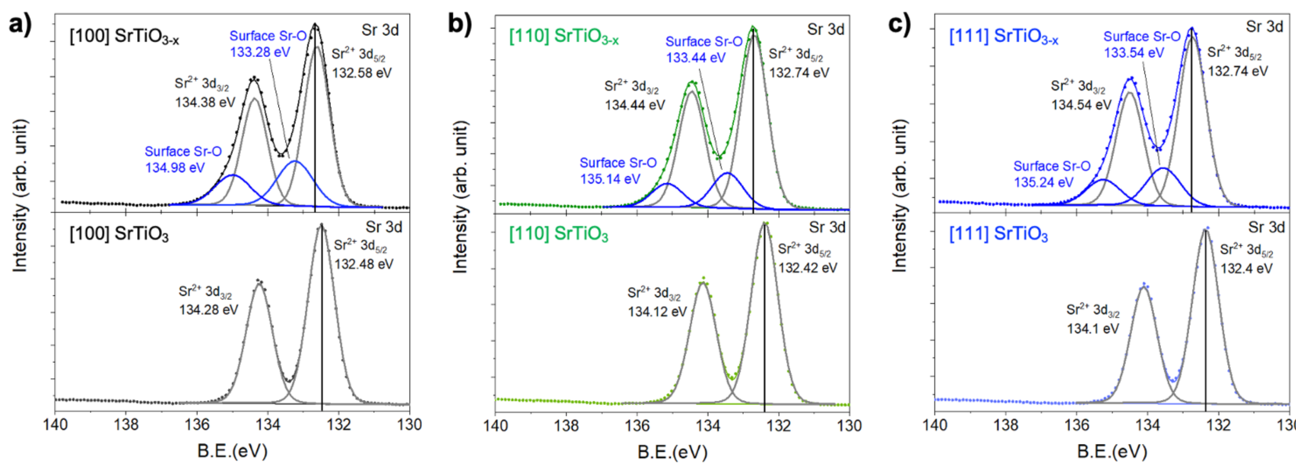

Figure S4. Sr 3d peak of a) (100), b) (110), and c) (111) facets of single crystal $SrTiO_3$ after (top) and before H_2 annealing (bottom).

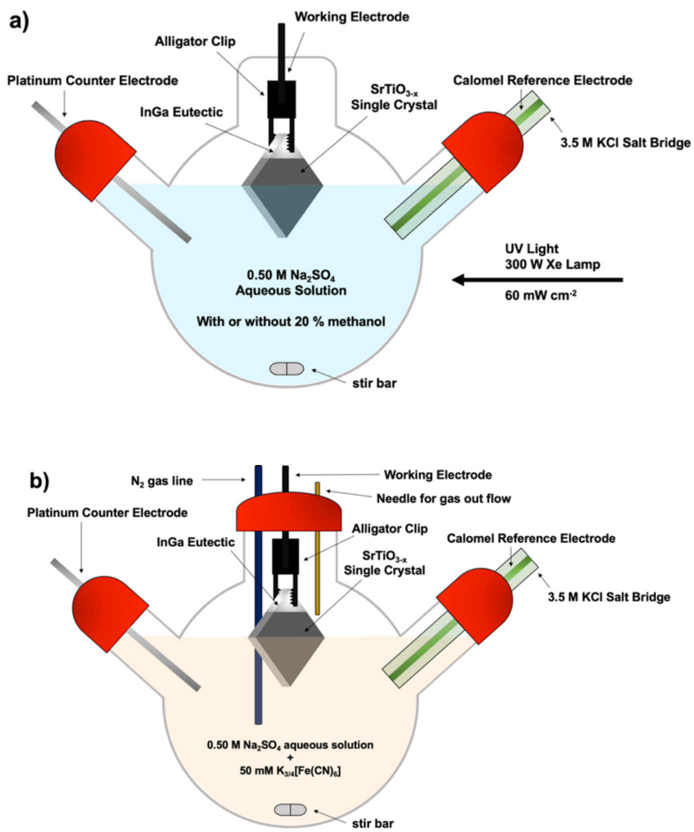

Figure S5. a) Three-electrode setup for PEC measurements. The working electrode is a $SrTiO_{3-x}$ single crystal with InGa eutectic coating in contact to the stainless steel alligator clip. A 0.50 M Na_2SO_4 aqueous electrolyte solution (pH = 5.95) exposed to open air is used under constant stirring. UV-light illumination occurs on the front side and is from a 300W Xe lamp with an intensity of 60 mW/cm^2 as measured with a GaN photodetector (220-380 nm). The working electrode area in contact with solution is 1.0 cm^2. As only the front side responds to illumination (**Figure S10**), the area of 0.50 cm^2 was used to calculate the photocurrent density. b) For Mott-Schottky (MS) measurements the electrolyte is a nitrogen-bubbled 0.50 M Na_2SO_4 aqueous electrolyte solution (pH = 5.95) with 50 mM equimolar $K_{3/4}[Fe(CN)_6]$. The solution was purged with N_2 gas for 30 minutes and bubbled with N_2 gas throughout all measurements with constant stirring at 200 rpm. No illumination was applied. The active area of the system is 1.0 cm^2 (both sides of the single crystal are in contact with the solution).

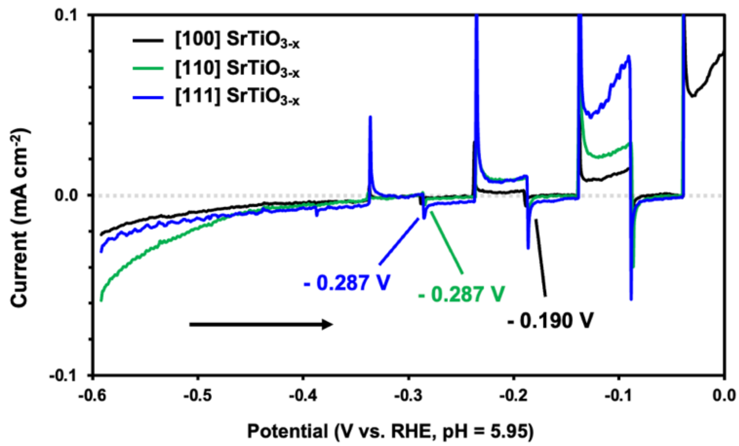

Figure S6. Magnified PEC scans for $SrTiO_{3-x}$ crystals under UV illumination (60 mW cm^{-2}) from Xe Lamp in a) 0.50 M Na_2SO_4 aqueous solution (pH = 5.95). The scan direction is from negative to positive potential as indicated by the horizontal arrow. The active electrode area is 0.50 cm^2. Onset potentials were estimated graphically by interpolation of the photocurrent.

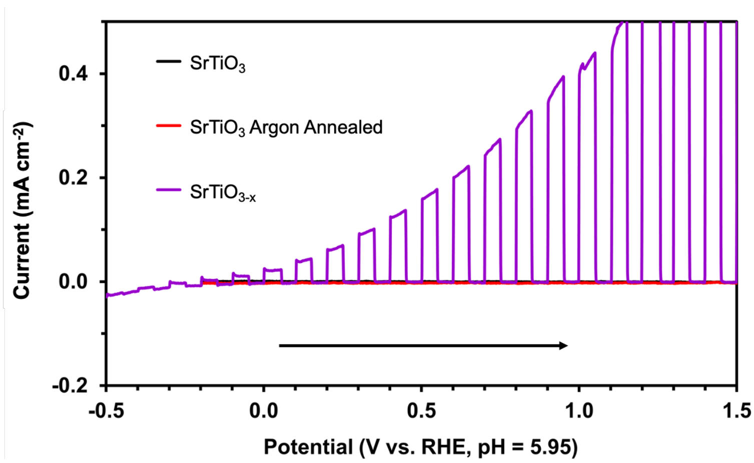

Figure S7. PEC scan in 0.50 M Na_2SO_4 aqueous solution under 60 mW cm^{-2} UV light illumination for as-received, Ar-annealed, and H_2-annealed $SrTiO_3$ single crystal with (111) exposed facet. The dataset was obtained from one single crystal sample. The sequence of measurements was as follows: 1st PEC measurement on the as-received $SrTiO_3$ sample. 2nd PEC measurement on sample after argon annealing (500°C). 3rd PEC measurements on crystal after H_2 annealing at 1,110°C. The argon annealing was an attempt to induce the formation of oxygen vacancies, but it was not successful, which is why H_2 annealing was utilized. The scan direction is from negative to positive potential as indicated by the horizontal arrow. The active electrode area is 0.50 cm^2.

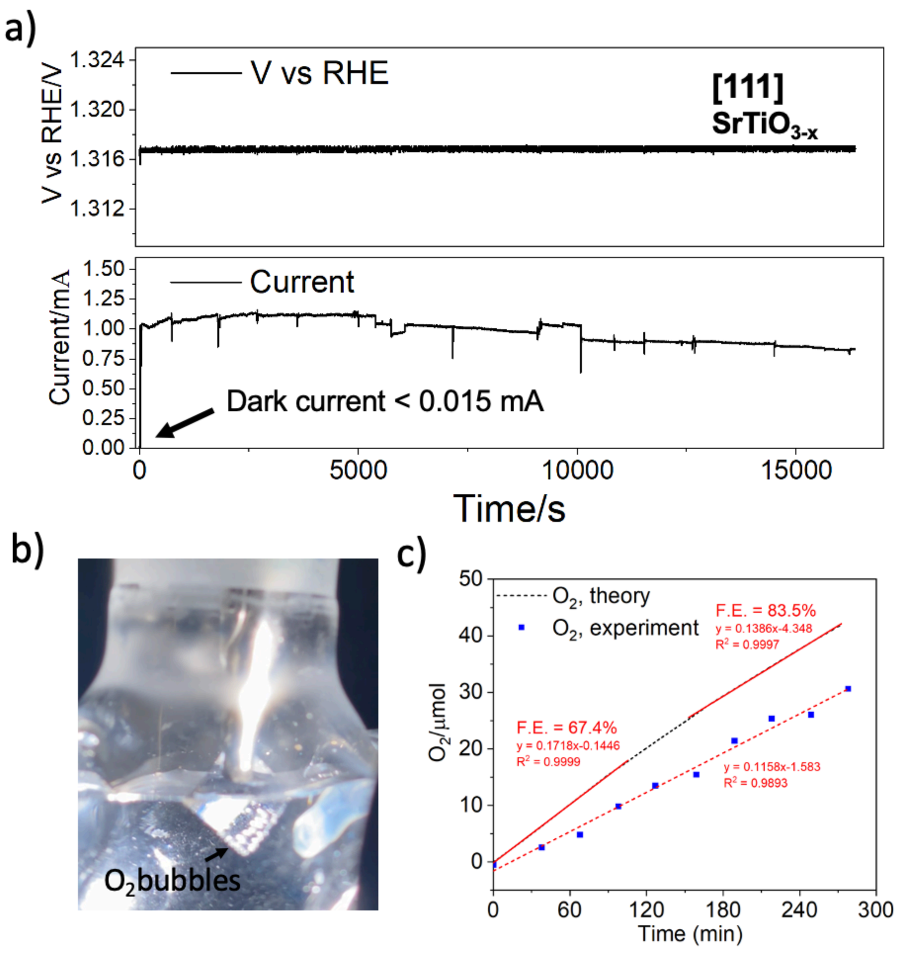

Figure S8. a) Chronoamperometry for H_2 annealed (111) $SrTiO_{3-x}$ single crystal at 1.33 V vs RHE in 0.50 M Na_2SO_4 aqueous solution under UV illumination (λ < 400 nm, 9 mW cm^{-2}) from a Xe Lamp. The active electrode area is 0.50 cm^2. Photocurrent variations are due to oxygen bubbles, see b) Photo of the working electrode. c) Faraday efficiency measurements (the solid line corresponds to theoretical O_2) were conducted by separating the counter electrode from the working electrode / reference electrode compartment using a salt bridge filled with aqueous 3.5 M KCl. Before the measurement, the electrolyte in the cell was degassed with argon to remove residual air. During measurement, samples were periodically removed from the headspace with a gas tight syringe, injected into a calibrated gas chromatograph (*Varian*), and quantified using a thermal conductivity detector. The data was adjusted for air contamination using the observed nitrogen contribution from air.

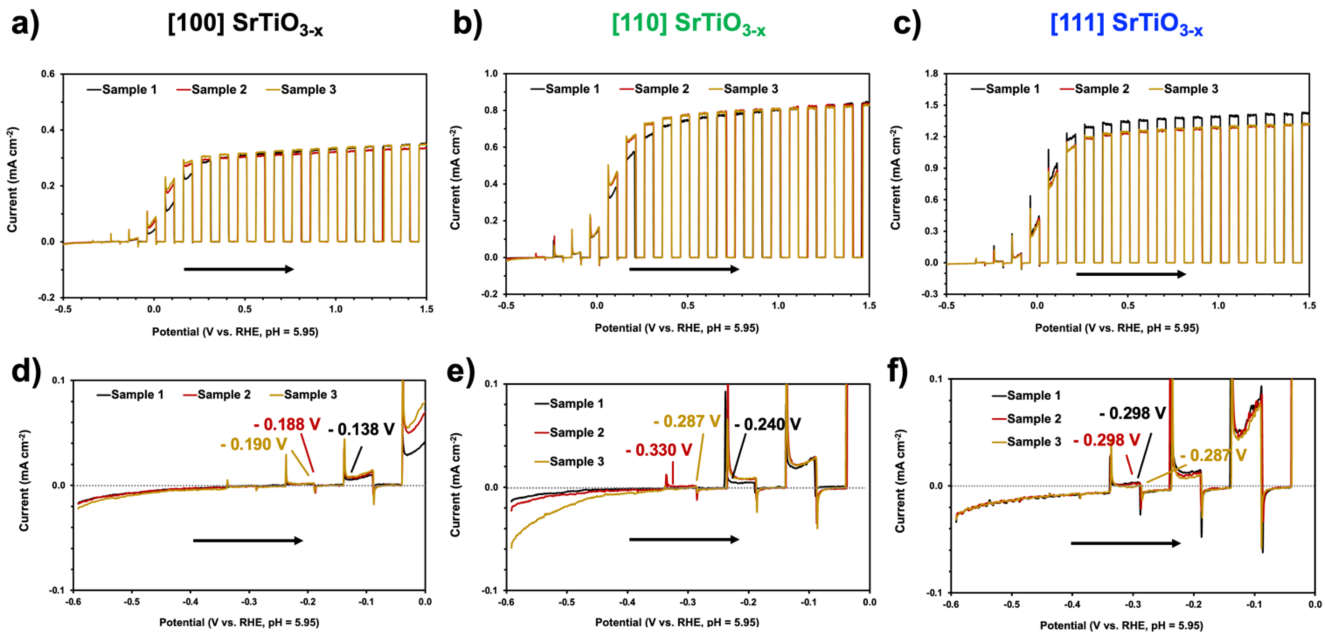

Figure S9. PEC for a) (100), b) (110), and c) (111) $SrTiO_{3-x}$ single crystals in 0.50 M Na_2SO_4 under UV light illumination (60 mW cm^{-2}) to determine the experimental error. The zoomed in plots reveal the photoonset potential, E_{ON}, for d) (100), e) (110), and f) (111) $SrTiO_{3-x}$ single crystals. Sample 3 is also featured in **Figure 4**. The scan direction is from negative to positive potential as indicated by the horizontal arrow. The active electrode area is 0.50 cm^2.

Table S2. Values and errors of photocurrent, photoonset, and photovoltage of three samples of (100, 110, 111) $SrTiO_{3-x}$ single crystals with different exposed facets corresponding to the data in **Figure S9**.

Crystal Orientation	**(100) $SrTiO_{3-x}$**			**(110) $SrTiO_{3-x}$**			**(111) $SrTiO_{3-x}$**		
Sample	**1**	**2**	**3**	**1**	**2**	**3**	**1**	**2**	**3**
Current (mA cm^{-2})	0.342	0.328	0.341	0.821	0.823	0.814	1.413	1.300	1.304
Photoonset (V RHE)	-0.138	-0.188	-0.190	-0.240	-0.330	-0.287	-0.298	-0.298	-0.287
Photovoltage (V)	1.37	1.42	1.42	1.47	1.56	1.52	1.53	1.53	1.52
Average Current (mA cm^{-2})	0.337			0.819			1.357		
Current Standard Deviation (absolute, %)	0.01, 2.97			0.00, 0.00			0.08, 5.89		
Average Photoonset (V RHE)	-0.172			-0.286			-0.294		
Photoonset Standard Deviation (absolute, %)	0.03, 17.4			0.05, 17.5			0.01, 3.40		
Average Photovoltage (V)	1.40			1.52			1.52		
Photovoltage Standard Deviation (absolute, %)	0.03, 2.14			0.05, 3.29			0.01, 0.65		

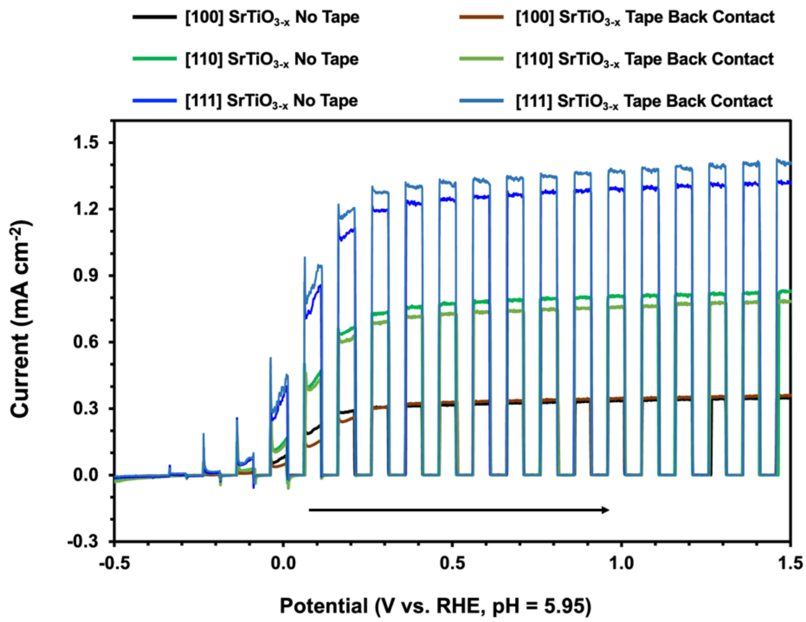

Figure S10. PEC of H_2-annealed $SrTiO_3$ single crystals to evaluate the effect of polyester tape at the back contact. Conditions: InGa contact, 0.50 M Na_2SO_4 aqueous solution under UV illumination (60 mW cm^{-2}) from Xe lamp. The addition of tape to the crystal back reduces the photocurrent by <10%. As >90% of the photocurrent is generated at the front side, current density calculations only need to consider the illuminated crystal front side. Scan direction is shown by the horizontal arrow.

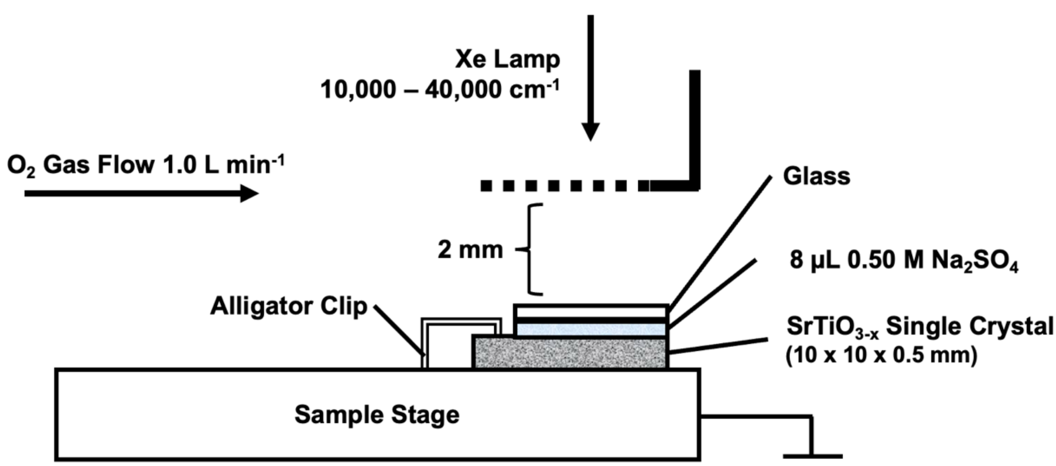

Figure S11. Surface photovoltage spectroscopy Measurement configuration.

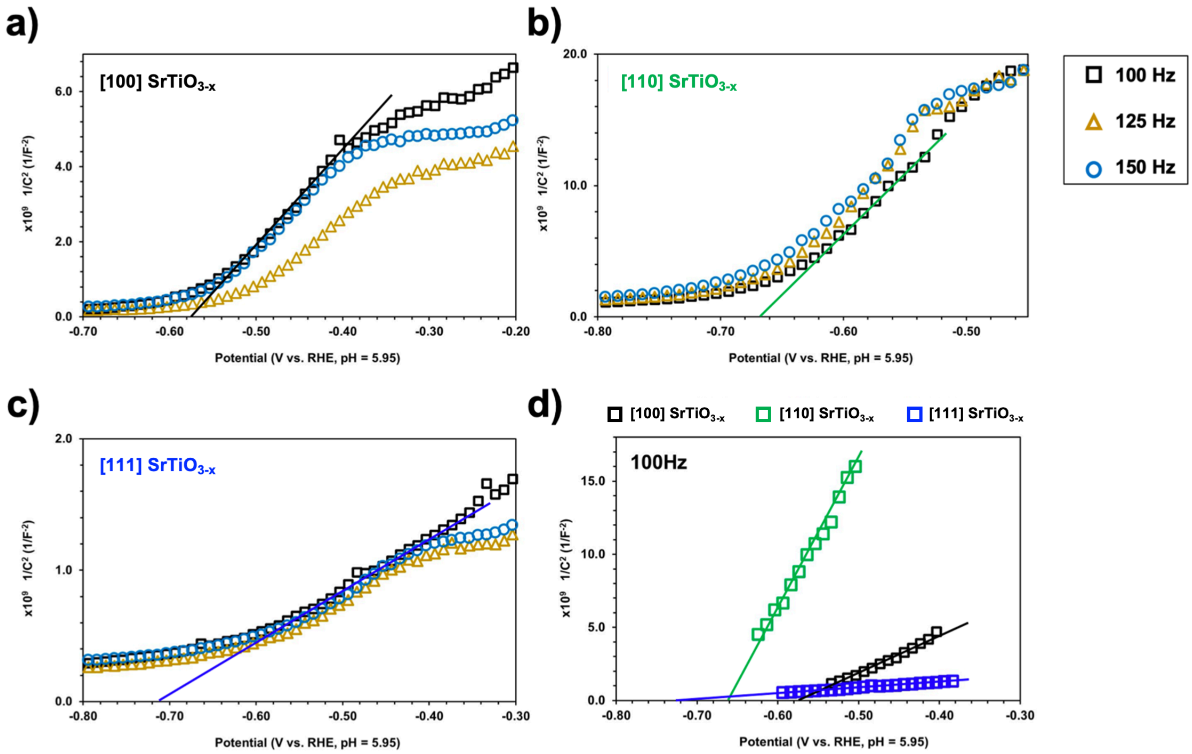

Figure 12. Mott Schottky plots at 100, 125, and 150 Hz in 0.50 M Na_2SO_4 aqueous solution (pH = 5.95) with 50 mM equimolar $K_{3/4}[Fe(CN)_6]$ under constant nitrogen purging without illumination for a) (100) $SrTiO_{3-x}$, b) (110) $SrTiO_{3-x}$, and c) (111) $SrTiO_{3-x}$ crystals. The crystal back is coated with InGa eutectic, as shown in **Figure S5b**. d) Comparison of the data at 100 Hz. Numerical values and calculation details are available in **Table S3.**

Table S3. Values obtained from Mott Schottky experiment and calculations for free electron density, N_D, flat band potential, E_{FB}, and conduction band edge, E_{CB}.

	(100) $SrTiO_{3-x}$			**(110) $SrTiO_{3-x}$**			**(111) $SrTiO_{3-x}$**		
Band Gap (eV)	3.2			3.2			3.2		
Dielectric Constant (ε)	300			300			300		
Thickness (m)	0.0005			0.0005			0.0005		
Area (A / m^{-2})	0.0001			0.0001			0.0001		
Effective Density of States (N_{CB} / cm^{-3})	8.00×10^{20}			8.00×10^{20}			8.00×10^{20}		
Frequency (Hz)	100	125	150	100	125	150	100	125	150
Potential (x-intercept)	-0.570	-0.542	-0.579	-0.666	-0.687	-0.699	-0.725	-0.712	-0.720
Flatband Potential (E_{FB} / V vs RHE)	-0.596	-0.567	-0.605	-0.692	-0.713	-0.725	-0.751	-0.738	-0.745
Slope ($C^{-2} \times 10^9$)	26.467	18.233	22.800	96.329	92.204	86.322	3.831	3.615	3.724
Free Electron Density (N_D / m^{-3})	1.78×10^{25}	2.58×10^{25}	2.06×10^{25}	4.88×10^{24}	5.10×10^{24}	5.44×10^{24}	1.23×10^{26}	1.30×10^{26}	1.26×10^{26}
Free Electron Density (N_D / cm^{-3})	1.78×10^{19}	2.58×10^{19}	2.06×10^{19}	4.88×10^{18}	5.10×10^{18}	5.44×10^{18}	1.23×10^{20}	1.30×10^{20}	1.26×10^{20}
Conduction Band Edge (E_{CB} / V vs RHE)	-0.69	-0.66	-0.70	-0.82	-0.84	-0.85	-0.80	-0.78	-0.79
Valence Band Edge (E_{VB} / V vs RHE)	2.51	2.54	2.50	2.38	2.36	2.35	2.40	2.42	2.41
Junctions	$SrTiO_3$ / O_2/H_2O			$SrTiO_3$ / O_2/H_2O			$SrTiO_3$ / O_2/H_2O		
E^0 (V vs RHE)	1.23			1.23			1.23		
Built-in Potential, V_{bi} (V)	1.83	1.80	1.83	1.92	1.94	1.95	1.98	1.97	1.97
Depletion layer width (nm)	58.0	47.8	53.9	114	112	108	23.0	22.3	22.6

Mott-Schottky measurements were performed using a Gamry Reference 600 Potentiostat at an applied frequency of 100-150 Hz. The space charge capacitance, C, varies with the applied potential over the depletion layer as determined by the Mott-Schottky equation:

$$\frac{1}{C^2} = (\frac{2}{\varepsilon\varepsilon_0 A^2 e N_D})(V - E_{FB} - \frac{k_B T}{e})$$

Here, e is the electron charge, ε is the dielectric constant, ε_0 is the permittivity of a vacuum, N_D is the free electron density, V is the applied bias, E_{FB} is the flatband potential, k is the Boltzmann constant, T is the temperature, and A is the surface area of the film in contact with the electrolyte. A plot of C^{-2} versus V yields a straight line with a slope than can be used to determine N_D.

Slope = ($2/e\ \varepsilon\ \varepsilon_0 N_D A^2$); Given ε of $SrTiO_3$ = 300, [1] A = 0.0001 m^2, $\varepsilon_0 = 8.8541 \times 10^{-12}$ C m^{-1} V^{-1}, and e = 1.60×10^{-19} C, for (111) $SrTiO_{3-x}$ at 100 Hz, the slope = 3.83×10^9 C^{-2} F^2 and the calculated N_D value of 1.23×10^{20} cm^{-3} was obtained. Using the Mott-Schottky equation, the flatband potential is determined from the intercept with the x-axis on the linear plot of C^{-2} versus V and converted from SCE to RHE. The x-axis intercept was -0.725 V RHE at pH = 5.95, and therefore E_{FB} is -0.751 V vs RHE.

The conduction band position, E_{CB}, is determined from the equation for a n-type semiconductor: $E_{CB} = E_{FB} + k_B T$ x ln (N_D / N_{CB}) where the effective density of states, N_{CB}, for doped $SrTiO_3$ was found to be approximately 8.00×10^{20} cm^{-3}. [2] Therefore, for (111) $SrTiO_{3-x}$ at 100 Hz, E_{CB} = -0.80 V RHE.

Strontium titanate has a band gap value of 3.2 eV [3] and the position of the valence band can be determined by adding the bandgap value to the conduction band position, E_{CB}. The valence band edge is therefore at approximately +2.40 V RHE at pH = 5.95.

The space charge region (SCR), or the depletion layer width, w, is calculated using the following formula:

$$w = \sqrt{\frac{2\varepsilon\varepsilon_0 V_{bi}}{e N_D}}$$

Here, e is the electron charge, ε is the dielectric constant, ε_0 is the permittivity of a vacuum, N_D is the free electron density, and V_{bi} is the built in potential.

References

1. H. E. Weaver, *Journal of Physics and Chemistry of Solids*, 1959, **11**, 274-277.
2. Q. Wang, T. Hisatomi, Y. Suzuki, Z. Pan, J. Seo, M. Katayama, T. Minegishi, H. Nishiyama, T. Takata, K. Seki, A. Kudo, T. Yamada and K. Domen, *Journal of the American Chemical Society*, 2017, **139**, 1675-1683.
3. J. G. Mavroides, J. A. Kafalas and D. F. Kolesar, *Appl. Phys. Lett.*, 1976, **28**, 241-243.