

## Supporting Information

### Optimised Heterojunctions Between [100]-oriented Rutile TiO<sub>2</sub> Ar-rays and {001} Faceted Anatase Nanodomains for Enhanced Photoelectrochemical Activity.

Alfonso Ballestas-Barrientos,<sup>a</sup> Xiaobo Li,<sup>a</sup> Samuel Yick,<sup>a, b</sup> Anthony F. Masters,<sup>a</sup> Thomas Maschmeyer<sup>a, \*</sup>

<sup>a</sup> Laboratory of Advanced Catalysis for Sustainability, School of Chemistry, The University of Sydney, Sydney 2006, Australia

<sup>b</sup> CSIRO Manufacturing, P.O. Box 218, Lindfield, NSW 2070 (Australia)

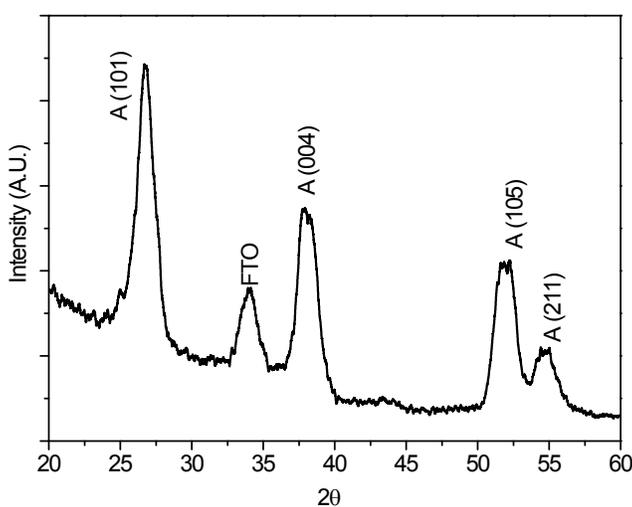


Figure S1. GIXRD pattern for T20

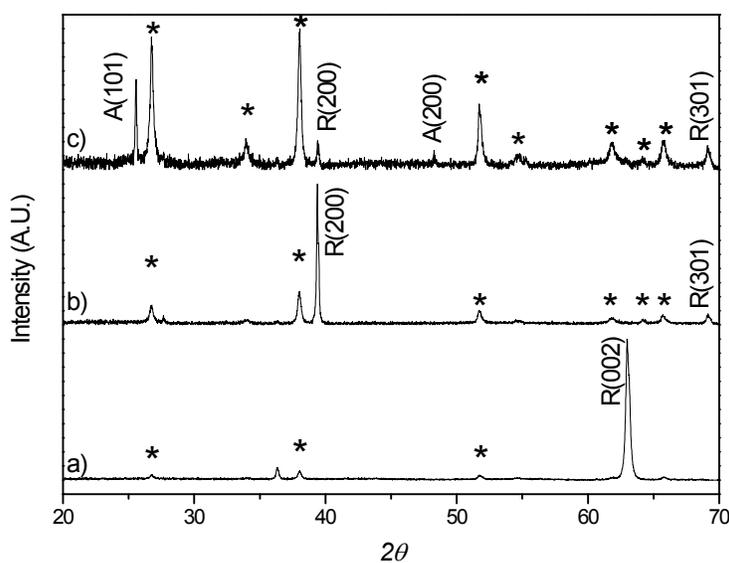


Figure S2. XRD patterns measured for T0-F, T5-F and T20-F (a, b, c respectively). Diffraction peaks denoted as “\*” correspond to the FTO substrate

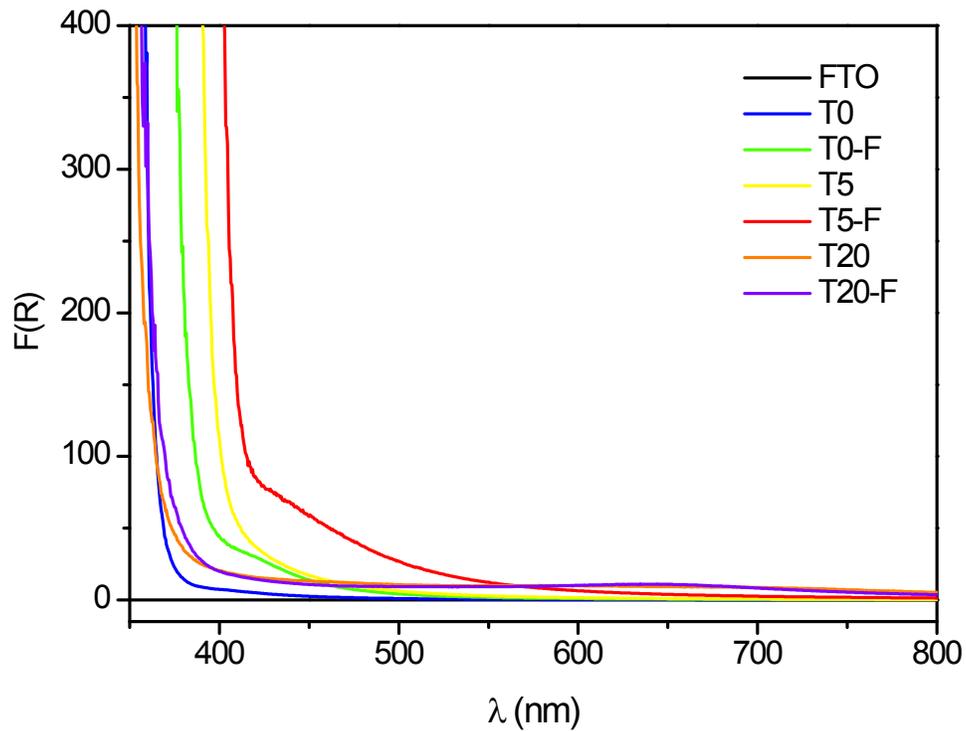


Figure S3. Optical properties of  $\text{TiO}_2$  films made with and without calcination. Optical measurements were made using the FTO substrate as a blank. The Kubelka-Munk function,  $F(R)$ , was used as an approximation of the optical absorbance of the samples based on their reflectance

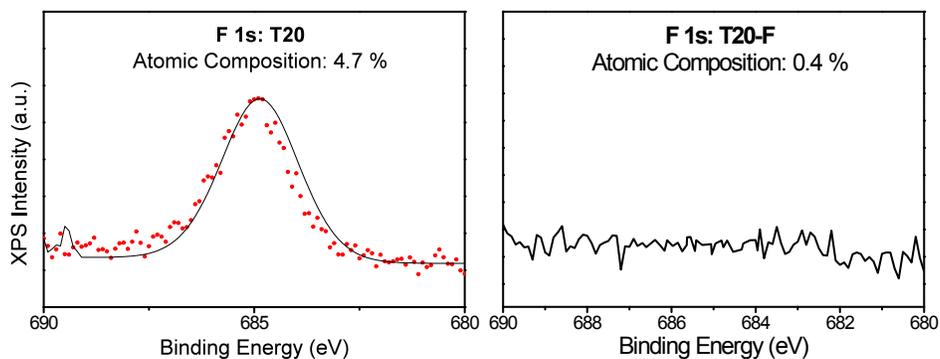


Figure S4. XPS spectra (narrow scan) for the F1s peak of samples T20 (left) and T20-F (right)

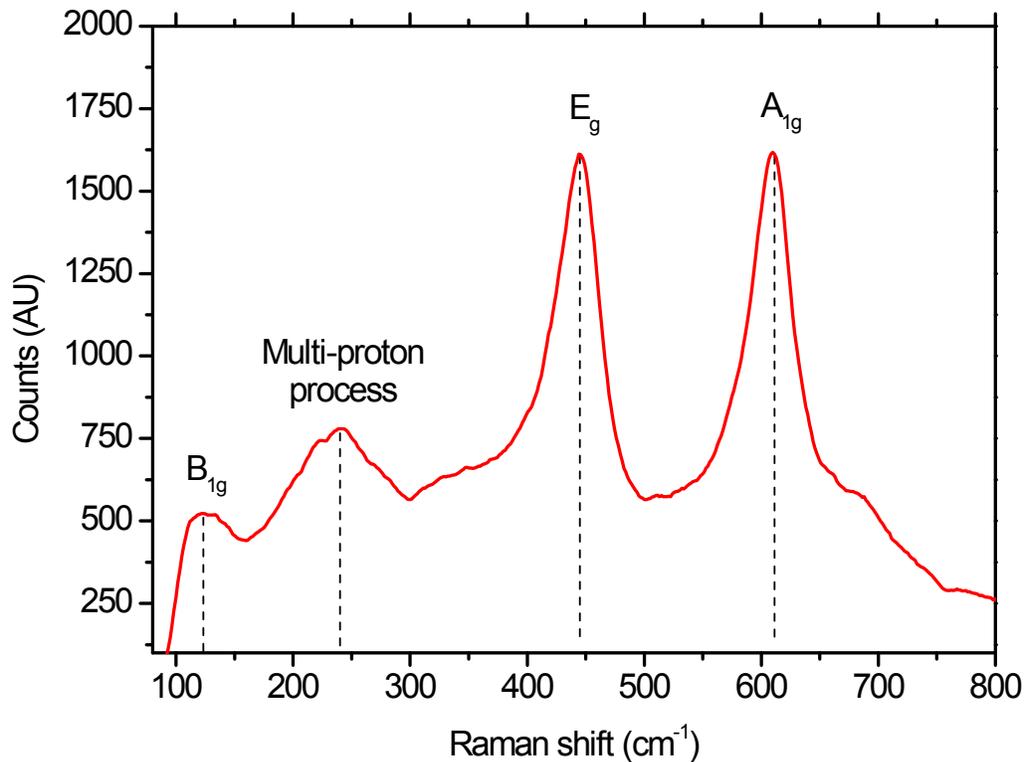
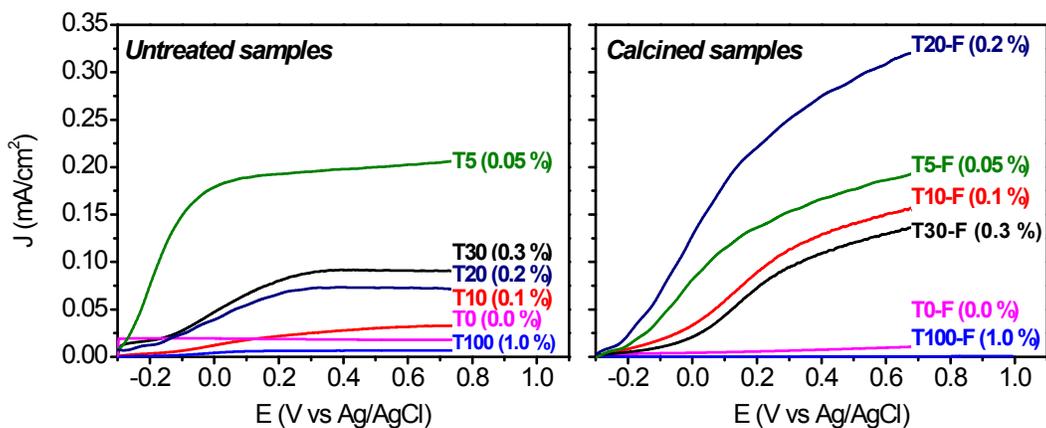


Figure S5. Raman spectrum of Rutile TiO<sub>2</sub> (Sample T5). The B<sub>1g</sub> peak originates from the symmetric bending vibration mode, while the E<sub>g</sub> and A<sub>1g</sub> peaks, used in this work to describe the surface energy, correspond to the symmetric stretching and anti-symmetric bending respectively.



S6. J-V plots of voltammograms at a light intensity of 100 mW/cm<sup>2</sup> for TiO<sub>2</sub> photoanodes prepared using a wide range of HF concentrations during the hydrothermal synthesis. Plots correspond to the samples measure prior to calcination (left) and post calcination (right).

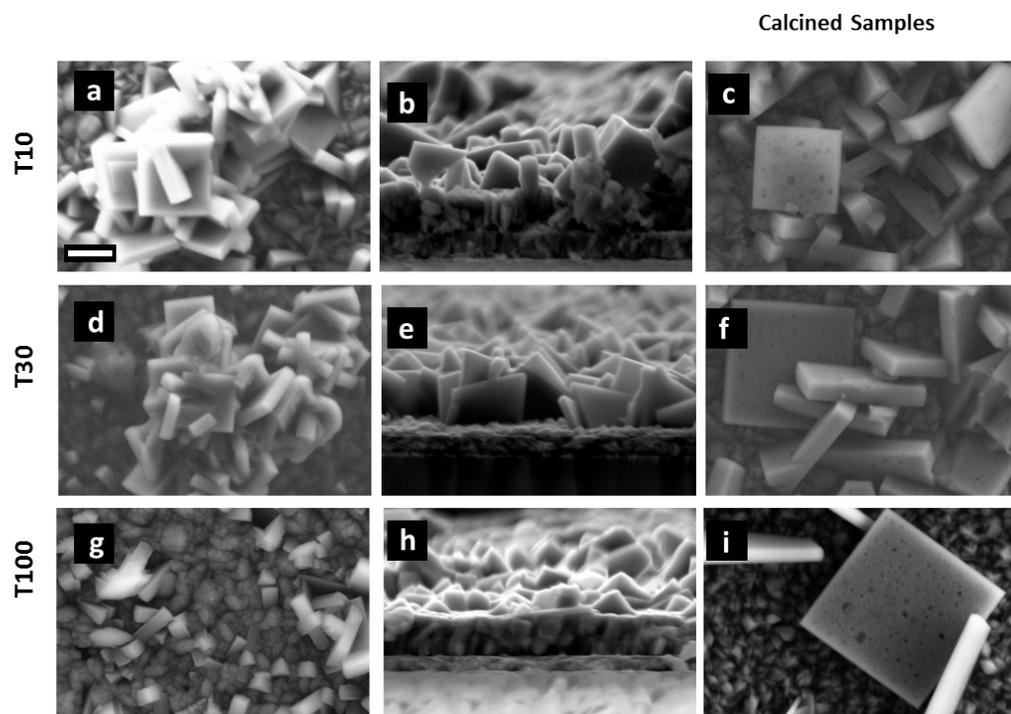


Figure S7. SEM images of TiO<sub>2</sub> films: T10 (0.1 % v/v HF, a-b), T30 (0.3 % v/v HF, d-e) and T100 (1.00 % v/v HF, g-h). Figures c, f and I correspond to the calcined T10-F, T30-F and T100-F samples respectively (Scale bar indicates 500 nm)

Table S1. Values of elements of an equivalent circuit<sup>a</sup> for TiO<sub>2</sub> films as measured in phosphate buffer (pH 7)

	T0	T5	T5-F	T20	T20-F
R1/Ω	67.06	88.55	83.50	52.83	72.77
Q1/(F·s <sup>a1-1</sup> )	3.29×10 <sup>-5</sup>	5.85×10 <sup>-4</sup>	6.96×10 <sup>-5</sup>	1.41×10 <sup>-4</sup>	6.69×10 <sup>-5</sup>
a1	0.91	0.87	0.85	0.66	0.57
R2/Ω	1.177×10 <sup>5</sup>	18.95	2742	1853	1878
Q2/(F·s <sup>a2-1</sup> )		3.97×10 <sup>-4</sup>	1.99×10 <sup>-5</sup>	1.35×10 <sup>-4</sup>	2.17×10 <sup>-13</sup>
a2		0.97	0.94	0.89	0.52
R3/Ω		1493	2132	1503	1635

<sup>a</sup>The equivalent circuit used to fit the impedance of the samples is shown in Figure 9c. Constant phase elements (CPEs) are denoted by “Q” and were used instead of capacitances to get a better fit, accounting for surface roughness and inhomogeneous chemical composition on the surface that cause deviation of the data from ideal behaviour. The “a” values (a1 and a2) indicate the degree of variation from the ideal resistor-capacitor (R-C) behaviour, where a value of 1 indicates an ideal capacitor. The fits were obtained using Zfit contained in the EC-Lab® v11.12 software and the quality of the fits was evaluated through the  $\chi^2$  value. A  $\chi^2$  value lower than 0.1 was considered to indicate a reasonable fit such that frequencies as well as shape agreement of the fitted points were assured.