

Supporting Information

For

Highly transparent $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ thin-film electrodes for ferroelectric-enhanced photoelectrochemical processes

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S1. Phase evolution with temperature of the Aurivillius $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ crystal phase

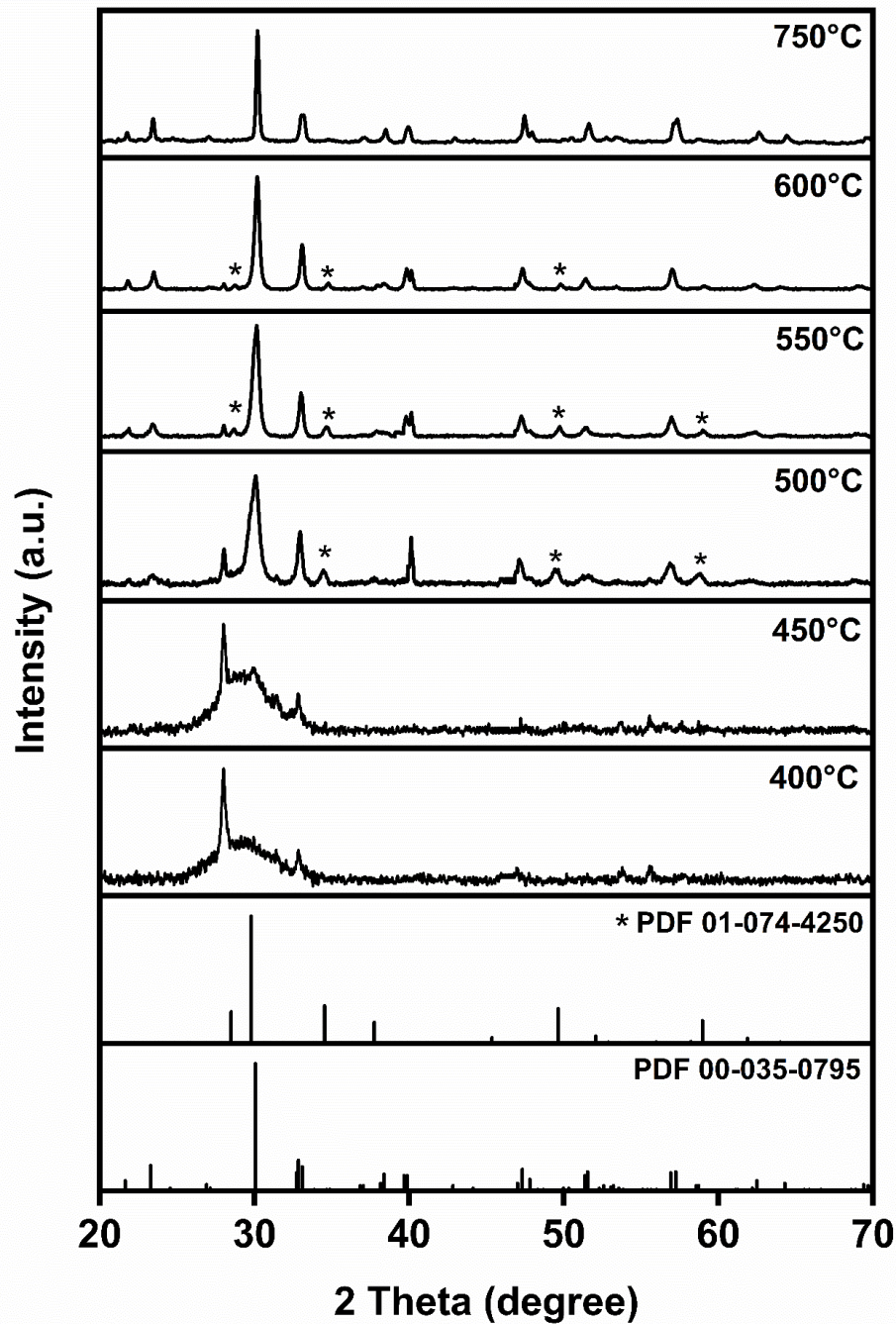


Figure S1. X-Ray diffraction patterns of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (PDF 00-035-0795) phase evolution at different temperatures. Asterisks indicate the presence of the pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ (PDF 01-074-4250)

The dried BiTO precursor (150°C) was subjected to *in situ* variable temperature X-Ray Diffraction in order to observe the $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase evolution with the changing of temperature (heating rate 5°C min⁻¹). As it is shown (**Figure S1**) the presence of the pyrochlore phase $\text{Bi}_2\text{Ti}_2\text{O}_7$ can be observed (as

a minority compound) since the BiTO amorphous precursor starts to crystallize, together with the desired Aurivillius $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ phase. However, at temperatures higher than 600°C , the pyrochlore intermediate starts to decompose, till it is not observed anymore (750°C).

It is however worth mentioning that these high temperatures necessary for the pyrochlore decomposition could not be employed for the fabrication of the BiTO photo-electrodes (*i.e.* layers samples) because of the increase in the electrical resistivity of the conducting FTO layer at temperatures higher than 500°C , not to mention the thermal stability of the underlying glass which would negatively affect the final uniformity of the spin-coated BiTO layers.

S2. Definition of the appropriate thermal treatment

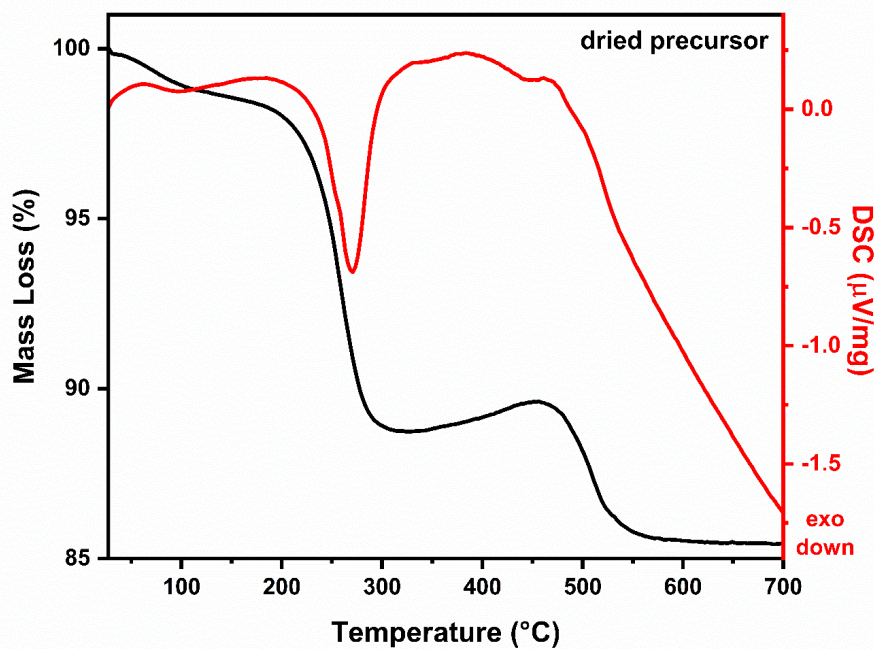


Figure S2. Thermal curve of the BiTO dried precursor.

In the first place, attention was given to the thermal annealing process with the aim of determining a proper heating cycle (*i.e.*, heating and dwelling temperatures and heating rate) to ensure the complete thermal decomposition of the precursors and obtain the desired BiTO crystal phase. More in detail, it is important to design a multi-step thermal process to avoid morphological defects such as micro cracks or blisters which can originate from the simultaneous

rapid evaporation and decomposition of all the compounds in the system¹. The tailored thermal treatment was defined by analyzing *via* a simultaneous thermal analyzer TGA-DSC a small amount of the amorphous glassy powder obtained by drying the BTO precursor solution at 150°C and then keeping the dried product at 100°C overnight to ensure the complete evaporation of the organic components. As reported in **Figure S2**, the dried precursor shows a first weight loss at around 100°C which is ascribable to the removal of absorbed water. After that, different thermal processes overlap in the region between 200 and 550°C, nevertheless, two different main slopes can be distinguished, the first one around 250°C and the second in the range 500 – 520°C. On this basis, the heating cycle reported in **Table S2** was defined. A short crystallization time of 30 minutes at 500°C (based on the literature) was therefore selected to minimize the stress on the FTO coated glass substrates².

Table S2. Optimized heating treatment of the dried photo-electrodes on the basis of the TGA-DSC analysis.

Temperature (°C)	Dwell (min)
250°C	30
500°C	30

S3. Characterization of the FTO-coated substrate

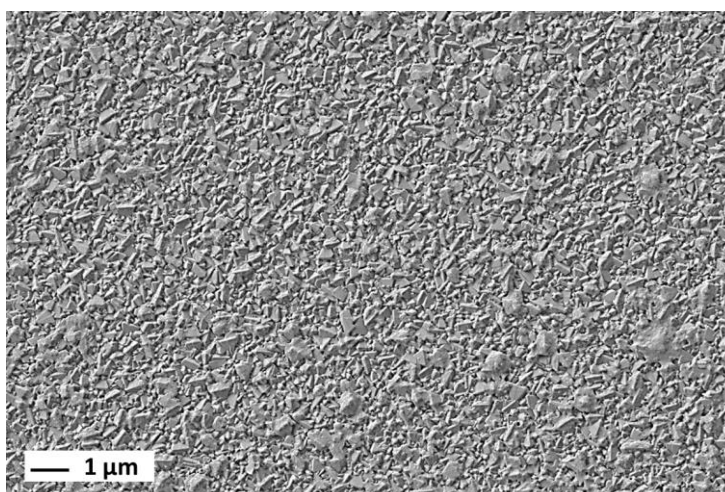


Figure S3.1. FE-SEM image of the bare FTO coated glass substrate.

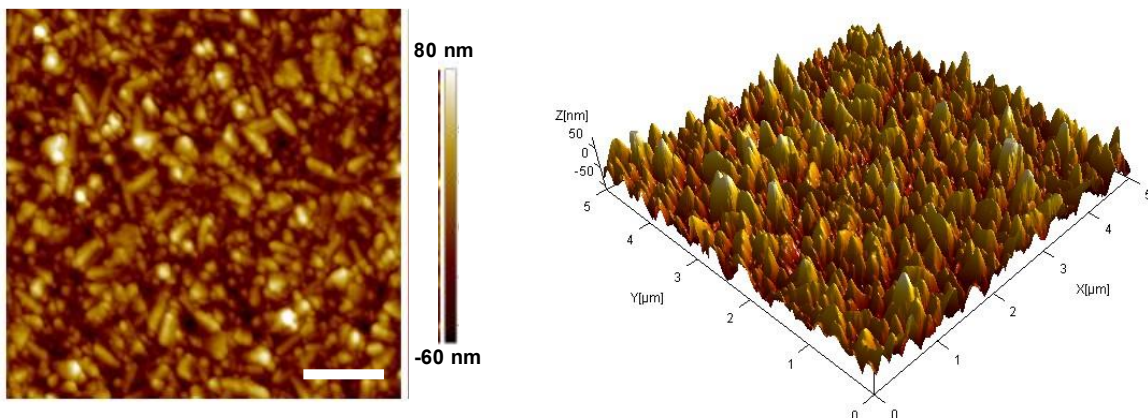


Figure S3.2. Representative atomic force microscopy (AFM) images of the topography of the bare FTO substrate. The scale bar is 1 micron.

Table S3. Roughness values extrapolated by the AFM analyses for the bare FTO substrate

Sample	R_a (nm)	R_q (nm)
FTO substrate	18 ± 1	23 ± 1

S4. LSV analyses

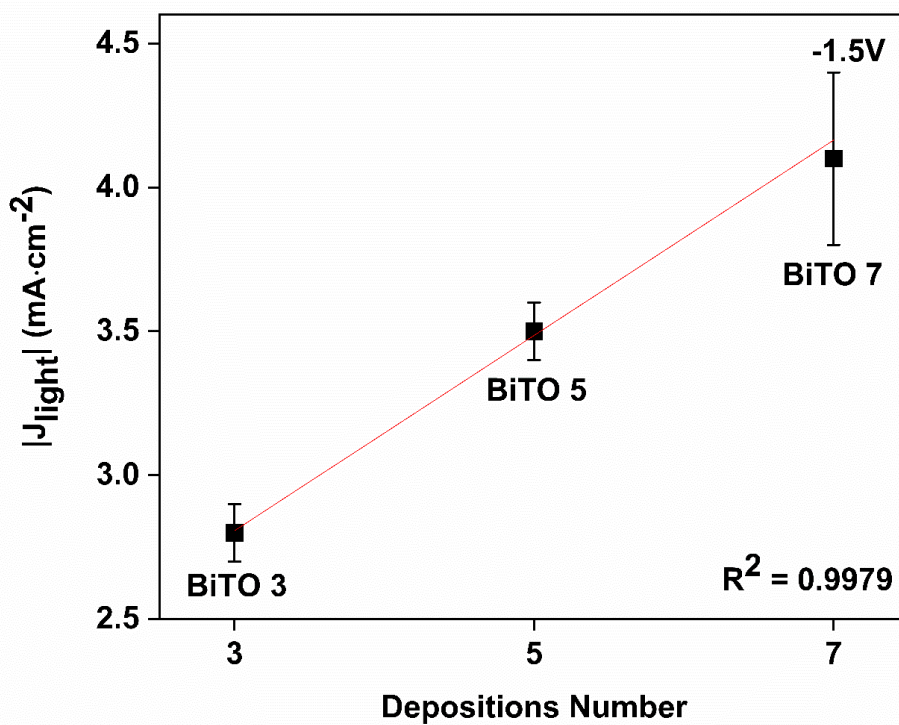


Figure S4.1. Density Current values under illumination conditions at -1.5 V vs Ag/AgCl as a function of the number of depositions.

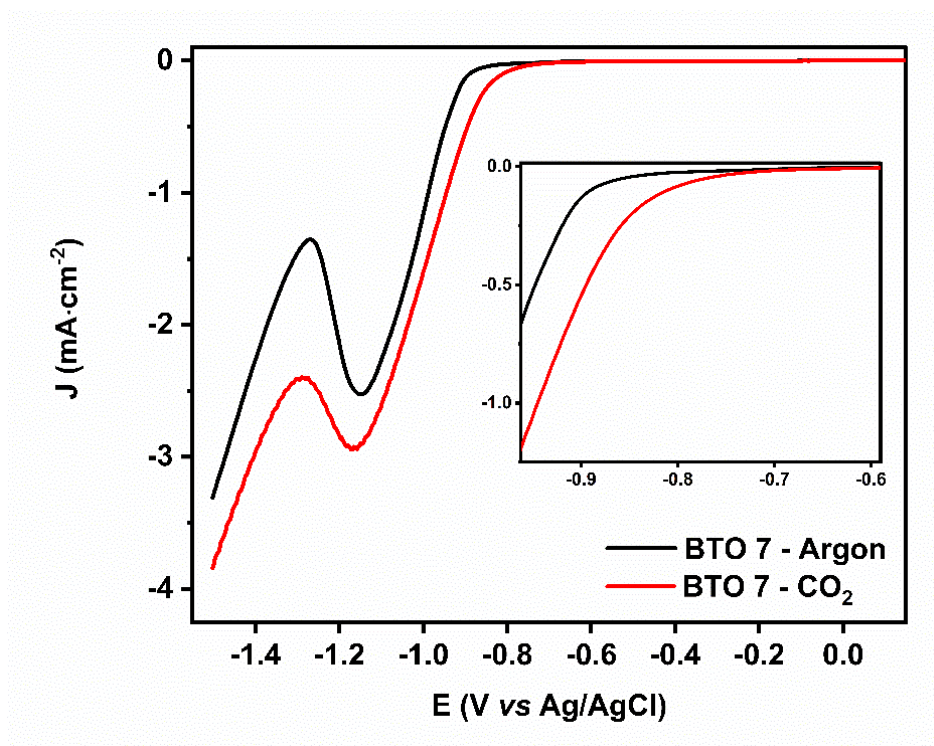


Figure S4.2. LSV curves of the 7 (BiTO7) deposition sample under illumination condition registered in 0.1 M KHCO₃ saturated with Argon (black curve) and carbon dioxide (red curve).

S5. Maximum Hydrogen amount evolved at potentials lower than -1.2 V (vs Ag/AgCl)

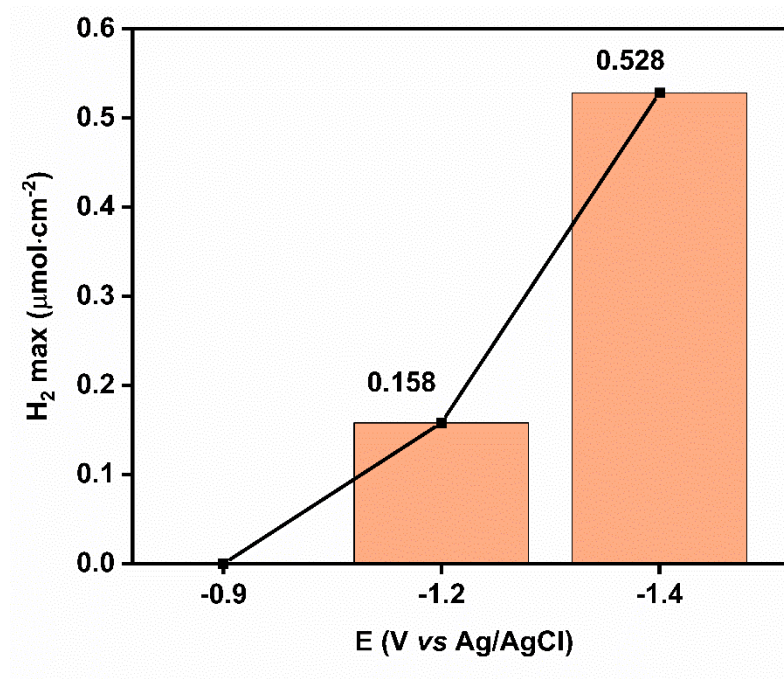


Figure S5. Maximum hydrogen amount produced by BiTO 7 *via* water splitting during 1 h chronoamperometric measurements under illumination (1 SUN, AM 1.5, 100 mW cm⁻²) at highly negative potentials in CO₂ saturated 0.1 M KHCO₃.

S6. Mott-Schottky analysis of BiTO 7

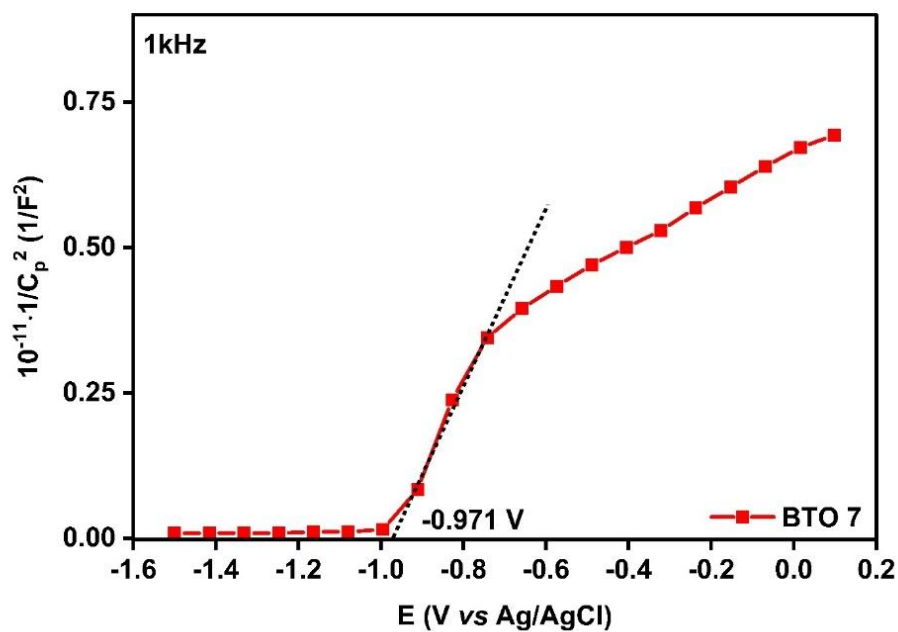


Figure S6. MS plot of the 7 depositions sample (BiTO 7) showing the extrapolated potential value used for the calculation of the layer flat-band potential.

Table S6. Thermodynamic potentials of main CO₂ and water redox reactions.

Reaction	E ⁰ (vs NHE, pH = 7)
CO ₂ + 2H ⁺ + 2e ⁻ → HCOOH	-0.61
CO ₂ + 2H ⁺ + 2e ⁻ → CO + H ₂ O	-0.53
CO ₂ + 4H ⁺ + 4e ⁻ → HCHO + H ₂ O	-0.48
2H ₂ O + 2e ⁻ → 2OH ⁻ + H ₂	-0.41
CO ₂ + 6H ⁺ + 6e ⁻ → CH ₃ OH + H ₂ O	-0.38
CO ₂ + 8H ⁺ + 8e ⁻ → CH ₄ + 2H ₂ O	-0.21
H ₂ O + 2h ⁺ → 1/2O ₂ + 2H ⁺	0.82

S7. Cross-sectional analysis of the BiTO 7 electrode

Table S7. Thicknesses of the BiTO 7 electrodes assessed *via* FE-SEM cross-sectional investigation.

Sample	Thickness (nm)	Average thickness (nm)
BiTO 7 – a	125	
BiTO 7 – b	132	130 ± 5
BiTO 7 – c	134	

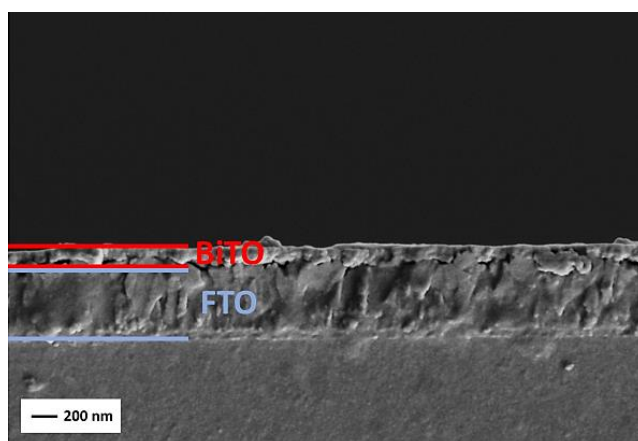


Figure S7. Representative FE-SEM cross-sectional micrograph of the BiTO 7 electrode showing a 132 nm-thickness $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ layer on top of the FTO-coated glass.

S8. Electrochemical Impedance Spectroscopy of BiTO 7 electrode at 0 and -0.8V (vs Ag/AgCl)

Table S8. Charge transfer resistance values (R_{CT}) extrapolated from the fitting of BiTO 7 electrodes in dark under different illumination conditions.

	R_{CT} (k Ω) at 0V (vs Ag/AgCl)	R_{CT} (k Ω) at -0.8 V (vs Ag/AgCl)
dark	$(1.2 \pm 0.3) \cdot 10^3$	30.8 ± 0.1
front illuminated	$(5.4 \pm 0.2) \cdot 10^2$	27 ± 2
back illuminated	$(4.2 \pm 0.2) \cdot 10^2$	18 ± 2

References

- 1 C. Gumiel, T. Vranken, M. S. Bernardo, T. Jardiel, A. Hardy, M. K. van Bael and M. Peiteado, *Boletín de la Sociedad Española de Cerámica y Vidrio*, 2018, **57**, 19–28.
- 2 P. Wollmann, B. Schumm and S. Kaskel, *Solid State Sciences*, 2012, **14**, 1378–1384.