Supporting Information

Multi-layered WO_3 nano-platelets for efficient photoelectrochemical water splitting: the role of the annealing ramp

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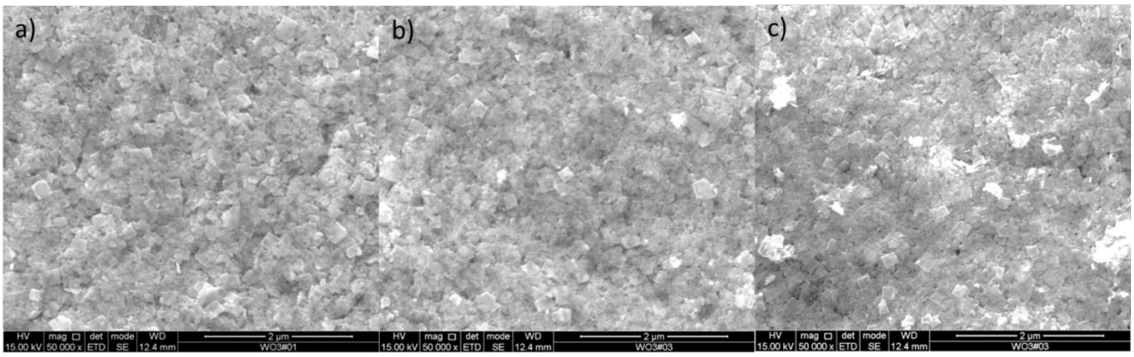

Figure S1. The top view SEM images for the set of samples annealed with a fast heating-ramp – 500 °C·h-1 with different thickness (*L*): 0.73 μm (a); 1.1 μm (b) and 1.9 μm (c).

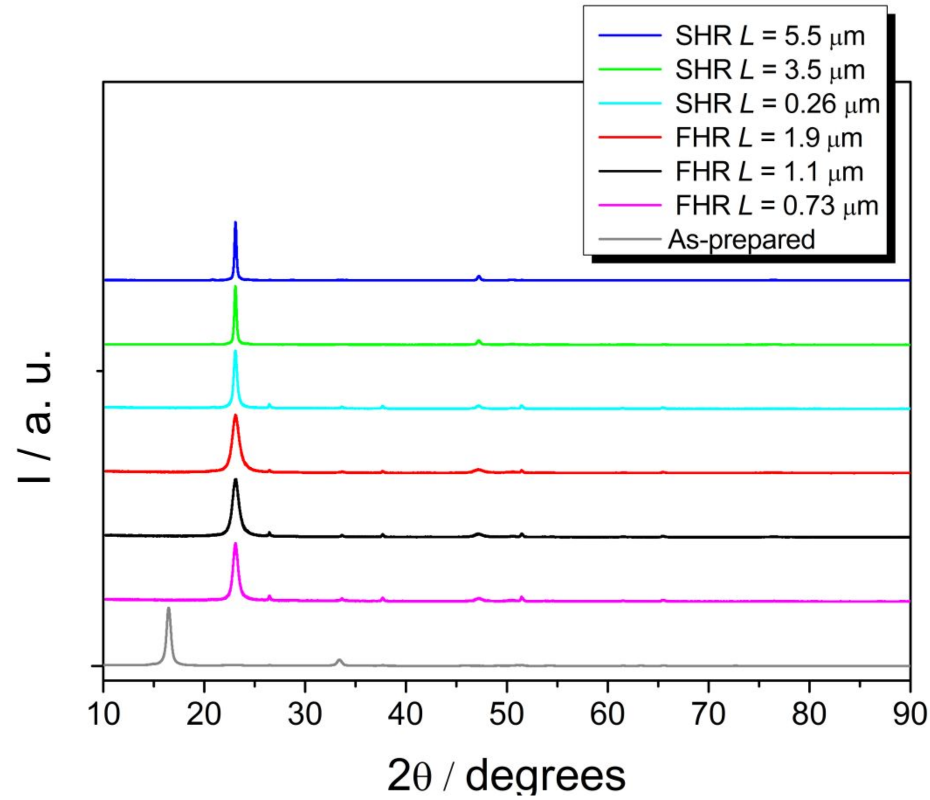

Figure S2. X-ray diffraction patterns spectra of WO_3 photoelectrodes in Bragg-Brentano focusing method: as-prepared and annealed for the fast heating-ramp and slow heating-ramp samples with different thicknesses normalized to the maximum peak.

Electrochemical Impedance Spectroscopy Analysis

Electrochemical impedance spectroscopy (EIS) measurements were performed using an Interface 5000E workstation (Gamry Instruments). The frequency range selected was 0.01 Hz – 100 kHz and the magnitude of the modulation signal was 10 mV. All the EIS experiments were performed at room temperature at an applied potential range of 0.75 V_{RHE} – 1.7 V_{RHE} under dark conditions. The measurements were conducted in a standard three-electrode configuration comprising an Ag/AgCl/Sat KCl electrode (Metrohm, Switzerland) as reference electrode, a platinum wire as counter-electrode, and the photoanode as working electrode, all immersed in a 3 M MSA aqueous solution. The experimental spectrum obtained for each studied sample was fitted to the simplified Randles electrical analogue by means of the ZView® software in the high frequencies range (100 Hz to 100 kHz). The Mott-Schottky analysis was conducted following Equation (S1):

$$\frac{1}{C_{SC}^{2}}=\frac{2}{\varepsilon_0\varepsilon_r e N_D A^2}\left(\left(V_E - V_{FB}\right)-\frac{kT}{e}\right) \qquad \text{(S1)}$$

where, ε_r is dielectric constant of the semiconductor (assumed 50 for WO_3[1]), ε_0 is the permittivity of space, k is the Boltzmann's constant, T the absolute temperature, e is the elementary charge, N_D is the donor density and V_E and V_{FB} are the applied voltage and the flat band potentials, respectively. By plotting $1/C_{SC}^2$ as a function of the applied bias potential, a straight line should be obtained; the donor density, N_D, can then be determined from the slope of this line, while the flat band potential, V_{FB}, value can be obtained by extrapolating the interception of the straight line with the axis of the applied potential [Figure S3 (a) and (b)] and Table S1.

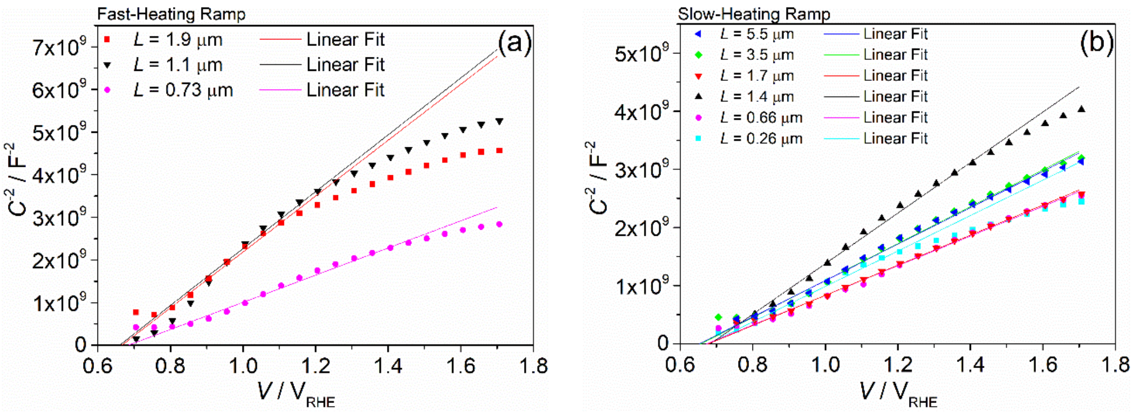

Figure S3. Mott–Schottky plots calculated from C_{SC} values determined from fitting the impedance spectra of WO_3 photoelectrodes: (a) annealed with a slow-heating ramp; and (b) annealed with a fast-heating ramp.

Table S1. Flat-band potentials (V_{FB}, in V_{RHE}) and Dopant densities (N_D, in 10^{21} cm^{-3}) both derived from linear fits in [[Figure S1 (a) and (b)] and according to Eq.S1.

	Sample	V_{fb} (V_{RHE})	N_D (10^{21} cm^{-3})
Fast-Heating Ramp	*L* = 0.73 μm	0.68	9.44
	L = 1.10 μm	0.66	6.65
	L = 1.90 μm	0.67	6.77
Slow-Heating Ramp	*L* = 0.26 μm	0.68	8.94
	L = 0.66 μm	0.67	9.79
	L = 1.40 μm	0.68	6.76
	L = 1.70 μm	0.68	10.31
	L = 3.50 μm	0.66	9.37
	L = 5.50 μm	0.65	8.55

Tauc plots

The optical band gaps for all the samples were determined using the Tauc formula:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad \text{(S2)}$$

where A is a constant, $h\nu$ is the incident photon energy, α the absorption factor, E_g is the band gap energy, and n is equal to 1/2 for an allowed direct transition, or 2 for an allowed indirect transition (for WO_3). The band-gap values can be determinate by the plot of $(\alpha h\nu)^{1/2}$ *vs.* $h\nu$ [Fig. S4 (a) and (b)]. The obtained values of E_g for the two groups of samples are displayed in Table S2.

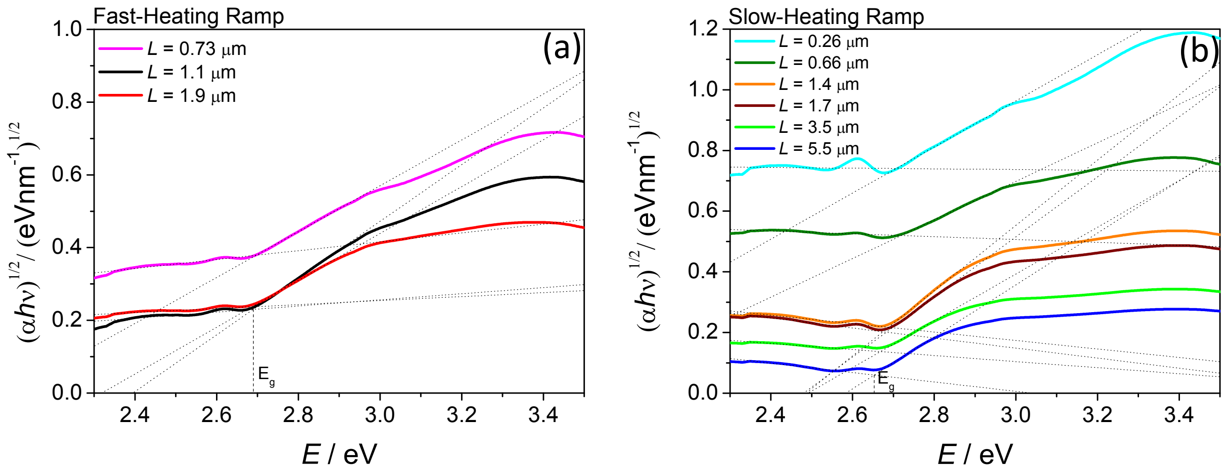

Figure S4. Tauc plots, *$(\alpha h\nu)^{1/2}$ versus $h\nu$*, of WO_3 photoelectrodes: (a) annealed with a fast-heating ramp and (b) annealed with a slow-heating ramp; *E*g is the band-gap.

Table S2. E_g band-gap both derived from linear fits from Figure S4 (a) and (b) and according to Eq.S2.

	Sample	E_g (eV)
Fast-Heating Ramp	L = 0.73 µm	2.70
	L = 1.10 µm	2.70
	L = 1.90 µm	2.69
Slow-Heating Ramp	L = 0.26 µm	2.71
	L = 0.66 µm	2.72
	L = 1.40 µm	2.69
	L = 1.70 µm	2.68
	L = 3.50 µm	2.67
	L = 5.50 µm	2.65

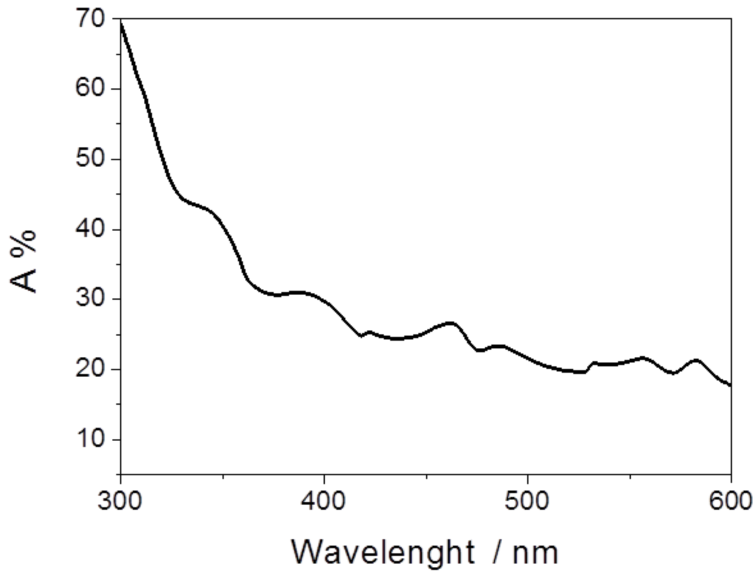

Figure S5. UV-Vis absorption spectra of the transparent TCO substrate.

REFERENCES

(1) Salje, E. and K. Viswanathan, Physical properties and phase transitions in WO_3. Acta Crystallographica Section A, 1975. 31(3): p. 356-359.