Photoelectrochemical Response of WO_3/Nanoporous Carbon Anodes for Photocatalytic Water Oxidation

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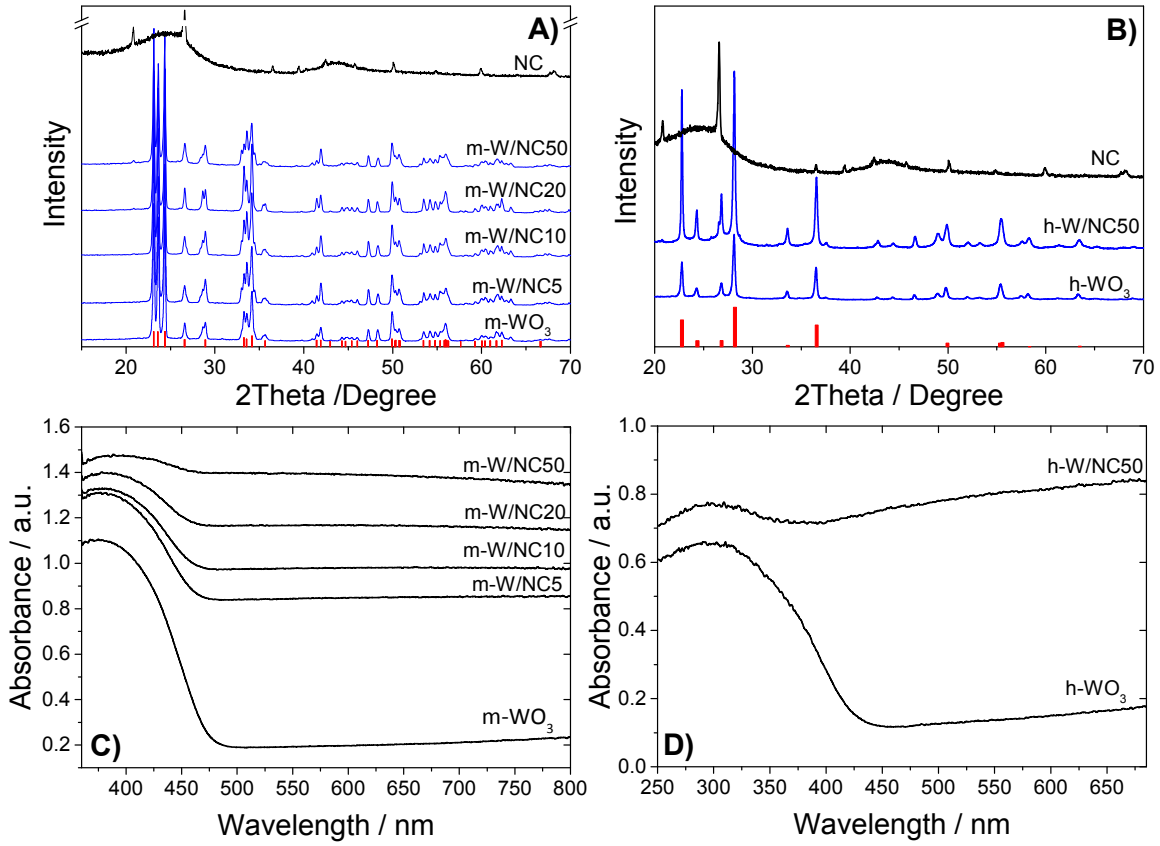

Figure S1. X-Ray diffraction patterns of (**A**) m-WO_3, NC and the m-WO_3/carbon mixtures; (**B**) h-WO_3, NC and the h-W/NC50, diffractograms are shifted for clarity; red bars indicate the standard pattern (JPDS-01-083-0950 and JCPDS-01-075-2187 corresponding to monoclinic and hexagonal lattice, respectively). Absorbance spectra of (**C**) m-WO_3 and the corresponding m-WO_3/carbon mixtures and (**D**) h-WO_3 and h-W/NC50.

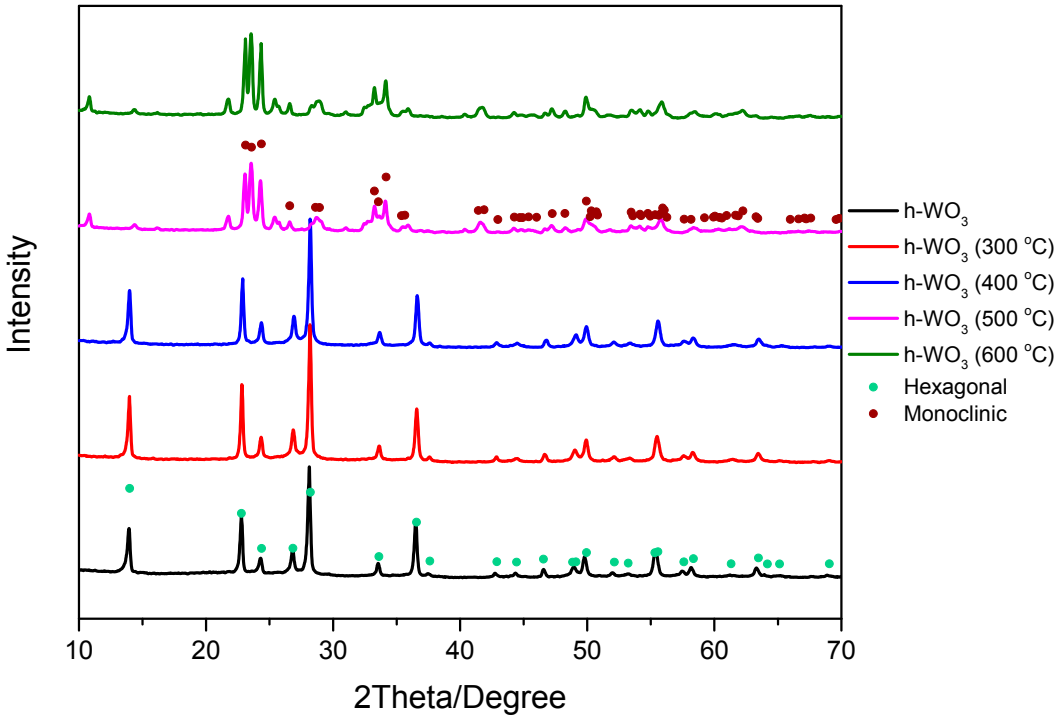

Figure S2. X-Ray diffraction patterns of h-WO_3 with increasing the calcination temperature; dots indicate the standard patterns corresponding to the hexagonal and monoclinic lattices.

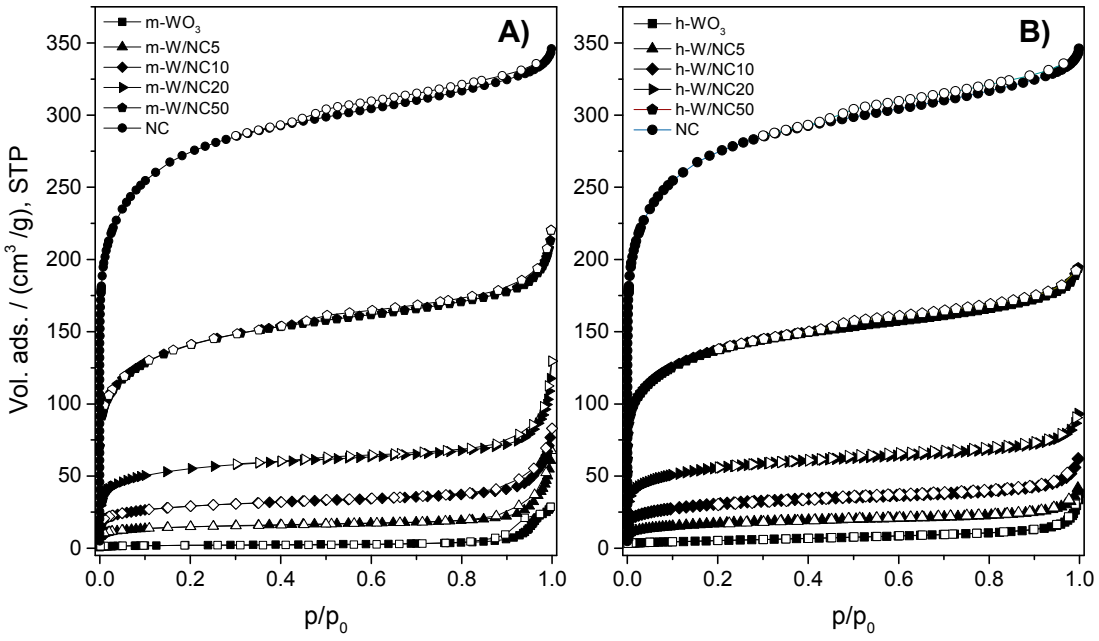

Figure S3. Nitrogen adsorption isotherms at −196 °C performed for the nanonoporous carbon and the semiconductor/carbon mixtures analysed (close symbols represent adsorption; empty symbols represent desorption).

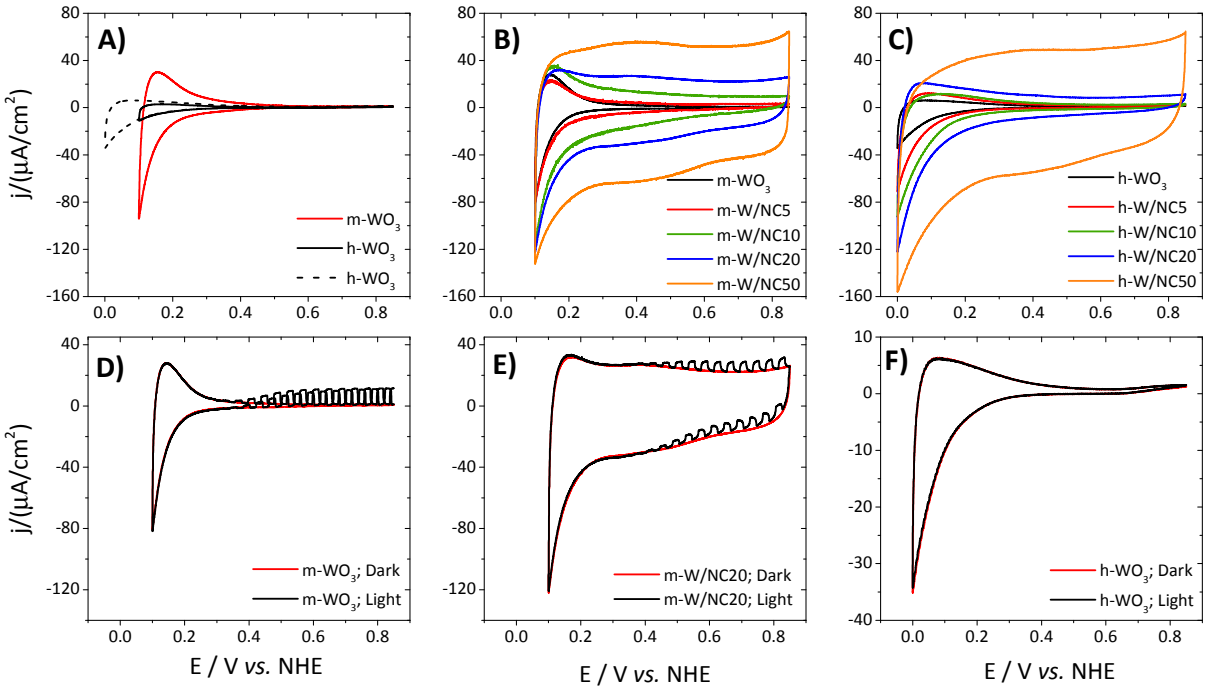

Figure S4. Cyclic voltammograms recorded at 20 mV/s of WO_3 and WO_3/carbon electrodes under (A–C) dark conditions and (D–F) and square-wave light perturbation at 371 nm (black line) for selected electrodes: (D) m-WO_3, (E) m-W/NC20 and (F) h-WO_3. Potentials are expressed vs. NHE.

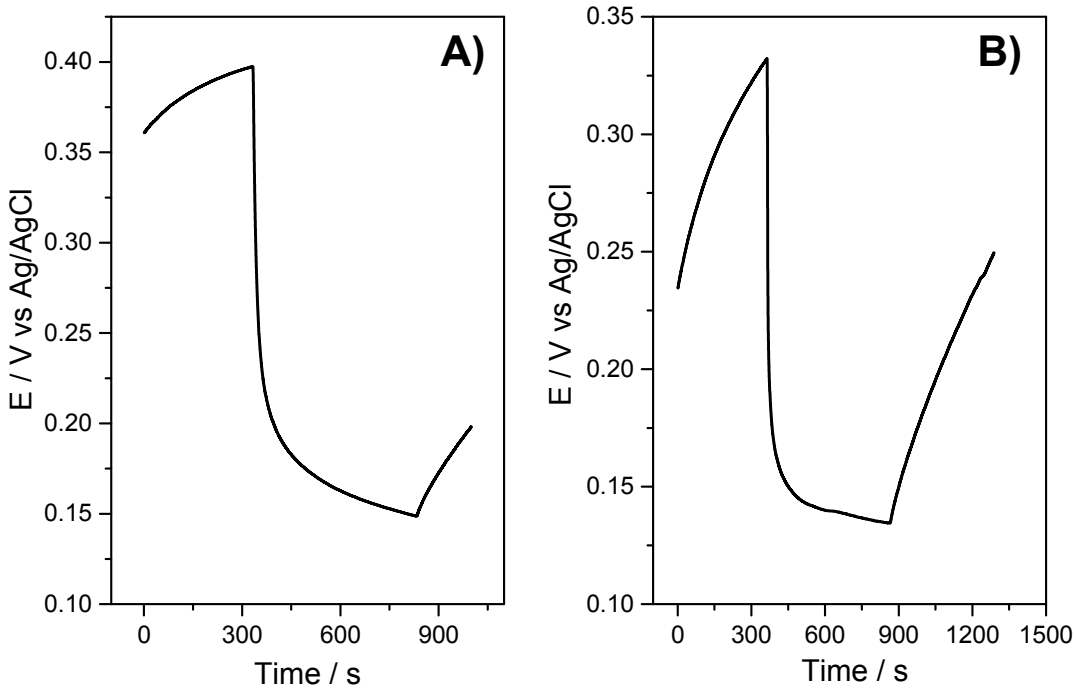

Figure S5. Evolution of the open-circuit potential (vs. Ag/AgCl) of (**A**) h-WO_3 and (**B**) m-WO_3 electrodes under illumination at 371 nm (photon flux of 3.4 x 10^{14} $cm^{-2}s^{-1}$).

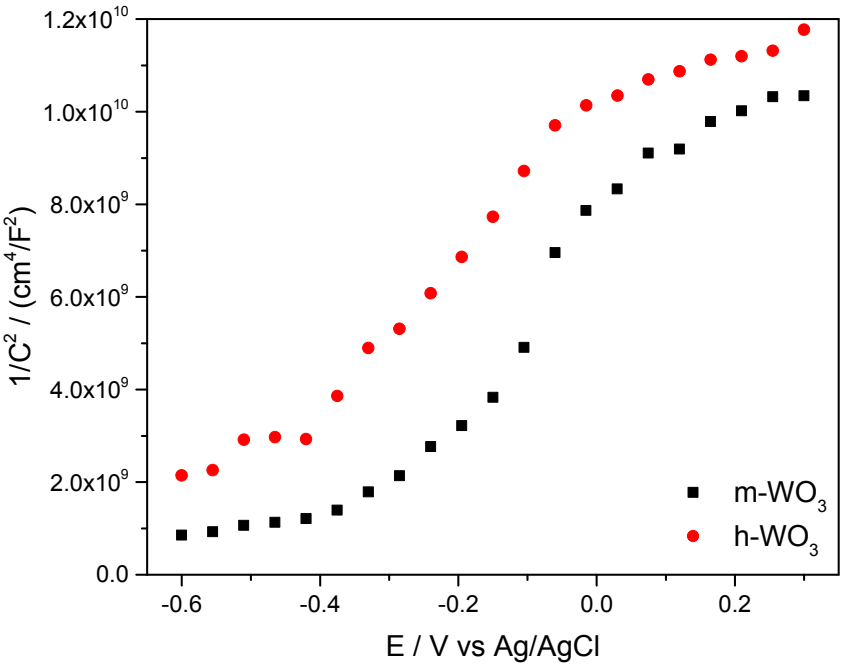

Figure S6. Mott-Schottky plots of WO_3 at 3.1 kHz under dark conditions in 0.5 M Na_2SO_4 pH 1.3.

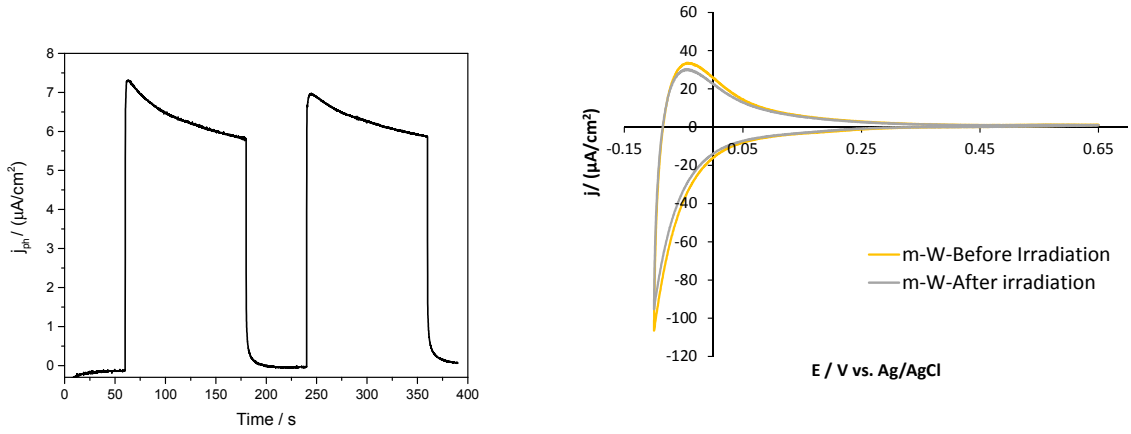

Figure S7. Consecutive transient photocurrent responses of m-W/NC10 electrode at 0.5 V vs Ag/AgCl (left). Cyclic voltammetry of m-W fresh and after irradiation (right).

Table S1. Main textural parameters of the semiconductors and the semiconductor/carbon mixtures obtained from the equilibrium nitrogen adsorption/desorption isotherms at −196 °C and surface pH.

	S_{BET} [m^2g^{-1}]	V_{total}[A] [cm^3g^{-1}]	Wo N_2[B] [cm^3g^{-1}]	S_{BET} (theoretical)[C] [m_2g^{-1}]	pH_{pzc}
h-WO_3	20	0.041	0.006	--	5.2
m-WO_3	6	0.038	0.002	--	4.3
h-W/NC5	62	0.057	0.026	71	n.a.
h-W/NC10	113	0.087	0.048	124	n.a.
h-W/NC20	207	0.134	0.074	223	n.a.
h-W/NC50	512	0.292	0.202	527	n.a.
m-W/NC5	56	0.077	0.019	59	5.2
m-W/NC10	108	0.104	0.037	110	5.9
m-W/NC20	205	0.160	0.070	212	6.0
m-W/NC50	524	0.315	0.187	520	7.2
NC	1033	0.520	0.320	--	8.9

[A] Total pore volume evaluated at p/p_0 ~0.99.

[B] Micropore volume evaluated using the Dubinin-Radushkevich method.

[C] Calculated from the S_{BET} of WO_3 and NC.

n.a. Not available