Supporting Information to:

Enhanced photopromoted electron transfer over a bilayer WO₃ heterojunction prepared by RF diodesputtering

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Figure S1. Emission spectrum of the 250 W iron halide mercury arc lamp (Jelosil HG200) measured by means of a compact CCD (Thorlabs CCS100 spectrometer).



Figure S2. Comparison of crystal unit cells of WO₃ (left) monoclinic (ICSD code 17003, a =7 .30 Å, b = 7.53 Å, c = 7.68 Å, $\alpha = \Box = 90^{\circ}$, $\Box = 90.9^{\circ}$, Space Group: P 21/n) and (right) orthorhombic (ICSD code 836, a = 7.341 Å, b = 7.57 Å, c = 7.754 Å, $\alpha = \Box = 0 = 90^{\circ}$, Space Group: Pmnb). Both cells contain 8 octahedrals; in the orthorhombic the four front ones overlap with the four in the back.



Figure S3. Monoclinic WO₃ supercells showing the (002), (020), (002) and (040) crystal planes.



Figure S4: (A) XRD patterns of (a) the pristine tungsten foil and (b) after annealing in air at 600 °C for 2 h. The peak positions and relative intensities of the cubic metal tungsten phase (ICSD code 653433) are reported at the bottom of the figure for comparison. The formation of a surface monoclinic WO₃ film after annealing is highlighted by the appearance of the reflections in the 0° < $2\Box < 50^{\circ}$ range. (B) Crystal unit cell of body centered cubic (bcc) metal tungsten (a = b = c = 3.1585 Å, $\alpha = \Box = 90^{\circ}$, Space Group: I m -3 m) showing the (011), (020) and (112) planes. The preferred orientation along the (020) plane may arise from the layered microstructure of the employed tungsten foil, as shown in the SEM image (C).



Figure S5. Determination of the electrochemically active surface area (ECSA) from double-layer capacitance measurements for 1L(1.7Pa) in 0.5 M Na₂SO₄. (a) Cyclic voltammograms measured in a 0.1 V region around the OCP (i.e., in a non-faradaic region) at different potential scan rates. (b) The cathodic and anodic capacitive currents taken at -0.1 V vs. SCE (= OCP) as a function of the scan rate. The double-layer capacitance C_{DL} of the system is the average of the absolute slope of the linear fits.



Figure S6. Deconvolution of PL emission spectra (excitation at 350 nm) of as prepared (i.e. before the 6 h-long photocatalytic water splitting test) WO₃ sputtered coatings, including the experimental (dots) and fitted (red line) spectra.



Figure S7. Experimental (grey line) and fitted (red line) XPS spectra of used 1L(1.7Pa) and 1L(3Pa) (i.e. measured after the 12 h-long irradiation water splitting test) in the (a) W 4f and (b) O 1s binding energy regions. In (a) the convoluted W $4f_{7/2}$ –W $4f_{5/2}$ doublets of W(VI) (blue lines) and of W(V) (green lines) are also shown. The fitting was performed using a Shirley background.



Figure S8. Evaluation of the bandgap energy of 1L(3Pa) and 1L(1.7Pa) from the IPCE curves measured at 1.0 V vs. SCE in 0.5 M Na₂SO₄ (pH 7) after the 6 h-long photocatalytic water splitting test, confirming the narrower E_g of the WO₃ coating deposited at higher pressure.



Figure S9. Photograph of the $4x4 \text{ cm}^2 2L(3+1.7\text{Pa})$ photoanode after the photocatalytic water splitting test, rinsed with Milli-Q water. Notice that the central irradiated round shape area displays a hydrophilic character (wettable surface), while the non-irradiated remaining part retains the original hydrophobicity (nonwettable surface).



Figure S10. Relation between the charge-transfer resistance (R_{ct}) and the oxygen production rate (r_{O_2}) according to Ohm's law: $R_{ct} = \Box / i_{ct} = (E_{appl} - E_{FB}) / (n F r_{O_2})$. Here, $E_{appl} = 1.24$ V vs. NHE, E_{FB} are those calculated from the Mott-Schottky plot, n = 4 is the number of electrons involved in water oxidation ($2 H_2O \Box O_2 + 4 H^+ + 4 e^{\Box}$) and F the Faraday constant. The slope of the straight line interpolating the experimental R_{ct} vs \Box/r_{O_2} values is very close to the expected (n F)⁻¹ = 2.591x10⁻⁶ mol C⁻¹. *Inverted heterojunction.