Supporting information

New Aspects of Improving the Performance of WO₃ Thin Films for Photoelectrochemical Water Splitting by Tuning the Ultrathin Depletion Region

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Figure S1. Photograph of the WO₃ thin film photoanode prepared via PLD.
The WO$_3$ thin films showed different preferential orientations when they were prepared under different partial pressures. When the oxygen pressure was higher than 10 mTorr, the crystallinity was optimized, which was confirmed by Raman. When the oxygen partial pressure was at 100 mTorr, the photocurrent became the highest.

Figure S2. a, XRD, b, Raman, c, LSV, and d, photocurrents at 1.23 V$_{\text{RHE}}$ for the WO$_3$ thin film samples prepared under different oxygen partial pressures.
Figure S3. SEM images for the WO$_3$ thin film samples prepared under different oxygen partial pressures.
Figure S4. a, UV-vis spectrum of the pristine WO$_3$ photoanode. b, XRD patterns, c, Raman spectra of the pristine WO$_3$, and reduced WO$_3$ samples (R-0, R-1, R-2, and R-3). d, XPS survey for a WO$_3$ thin film sample.
Figure S5. (a) The equivalent circuit used to model the electrochemical impedance of the cell. (b) Flat band indications by EIS results. R1, R2, and R3 are about 0.77, 0.79, and 0.81 VRHE respectively. These values are in the range of the published results. ¹ ⁴

The impedance of the electrochemical cell (Z) was measured under dark conditions at a series of electrode potentials, in the frequency (f) range 10² to 10⁵ Hz. To extract the space-charge region capacitance from the experimental impedance, the electrochemical cell was modeled by the equivalent circuit shown in Figure S6. The two current components flow together through the electrolyte solution and the electrical contact to the working electrode, which were represented by a series resistance R3. The current passing through the cell contributes in parallel to the faradic process that is represented by the charge transfer resistance R2 and nonfaradic interface charging that is represented by C2 (C_sc), the capacitance per unit area of the aqueous interface. The capacitance C includes the space-charge region capacitance C2 (C_sc) and the double-layer capacitance C1 (C_dl) in series, 1/C = 1/C_sc + 1/C_dl. The experimental data shown in Figure 5a is then fit using the EIS Spectrum Analyzer (ZVIEW2), software for analysis of impedance spectrum.
Given that the photogenerated majority carriers can diffuse in opposition to the electric field to the interface and therefore reduce the photocurrent. To describe this behavior, the electron collection efficiency can be determined by the following equation,

\[ \eta_e = \frac{1}{(1 + \frac{\mu_n E_0}{\nu_c})(1 + \frac{E_0 e}{\alpha kT})} \]

where \( \mu_n \) is the electron mobility, \( E_0 \) the absolute magnitude of the electronic field at the interface, \( \nu_c \) the effective collection velocity, and \( e, \alpha, kT \) as the previous definition. This expression represents the collection efficiency for photogenerated electrons that diffuse to the interface rather than drift to the back-contact side. In the depletion approximation, the absolute magnitude of the electronic field at the interface \( E_0 \) is given by,

\[ E_0 = \sqrt{\frac{2eV_{bi}N_D}{\varepsilon \varepsilon_0}} \]

where \( e, \varepsilon, \varepsilon_0 \) and \( N_D \) follow the previous definition, and \( V_{bi} \) the built-in voltage. Therefore, by increasing donor density \( N_D \), \( E_0 \) can be increased with pertinence. Figure S6a showed that \( E_0 \) can be enhanced significantly with enhanced \( N_D \) for the WO3 photoanodes after reduction treatment. Therefore, the electron collection efficiency can be reduced by increasing the donor density. By the mild reduction in our case (Fig. S7b), the electron collection efficiency can be suppressed effectively.
Compared to the EIS equivalent model for dark condition (Fig. S5, ESI), this equivalent circuit model (Fig. S7, ESI) additionally contains a chemical capacitance ($C_{ss}$) representing the chemical capacitance of the traps, a trapping resistance ($R_{trap}$) representing the trapping/detrapping resistance of electrons that go from the conduction band to the traps at the surface, and a charge-transfer resistance ($R_{ct}$) from the traps.

The current passing through the cell contributes in parallel to the faradic process that is represented by the serial resistance $R_1$, trapping resistance $R_2$ ($R_{trap}$), charge transfer resistance $R_3$ ($R_{ct}$) and nonfaradic interface charging that is represented by $C_1$ ($C_{bulk}$ or $C_{sc}$), double layer capacitance $C_3$ ($C_{dl}$), surface trap capacitance $C_2$ ($C_{ss}$).
Figure S8. a. Current density vs. potential under back-side (SE) AM 1.5 illumination for the WO$_3$ photoanodes R-0, R-40, R-60, and R-80. The vertical line indicates the thermodynamic potential for oxygen evolution (1.23 $V_{\text{RHE}}$). b, The photocurrent of the WO$_3$ photoanodes (R-0, R-1, R-2, and R-3) at 1.23 $V_{\text{RHE}}$, and the relative enhancements for the reduced WO$_3$ photoanodes (R-1, R-2, and R-3). c – d, back-side (BE) IPCE as a function of excitation wavelength potential, for the R-0 (Pristine) and R-40 (reduced for 200s) WO$_3$ photoanodes. Both the panels share the same color scale. The dashed lines are contours for corresponding IPCE values in percentage. e, back-side (SE) IPCE measurements for the WO$_3$ photoanodes (R-0, R-40, R-60, and R-80), carried out at 1.23 $V_{\text{RHE}}$. The characterization of the photoanodes were conducted in 0.5 M H$_2$SO$_4$ electrolyte.

The $J – E$ curves under illumination from the back of the WO$_3$ photoanodes R-0, R-1, R-2, and R-3 (back-side, SE) were plotted in Fig.5a. Different from the $J – E$ curves under EE illumination, the photocurrents of each WO$_3$ photoanodes (R-0, R-1, R-2, and R-3) were much lower than that of the photoanodes under SE illumination, and they were all close to 0.5 ~ 0.6 mA/cm$^2$ at 1.23 $V_{\text{RHE}}$. For example, the photocurrent of R-1 at 1.23 $V_{\text{RHE}}$ was only 0.57 mA/cm$^2$, slightly higher than that of R-0. The photocurrents of R-2 and R-3 at 1.23 $V_{\text{RHE}}$ decreased as the reduction time increased. The subsequent IPCE measurements was plotted in Fig. 5e with back-side (EE) IPCE at 1.23 $V_{\text{RHE}}$ versus excitation wavelength. The IPCE of the reduced WO$_3$ photoanodes (R-1, R-2, and R-3) presented significant enhancement in the range from 300 to 360 nm. However, in the range from 360 to 500 nm, the IPCE for all the four WO$_3$ photoanodes (R-0, R-1, R-2, and R-3) did not present obvious differences. Nonetheless, the SE and EE PEC performances and IPCE attributable to excitation from the wavelengths did not exhibit a simple correction with the reduction time on the WO$_3$ photoanodes, which, however, is consistent with the XPS and Mott-Schottky study analysis described below.

The back-side (SE) IPCE presented no enhancement in the longer wavelength range from 360 to 500 nm. This resulted from the recombination sites in the subsurfaces beyond the SCR for R-1, R-2, and R-3 suppressed and quench the photogenerated charge carriers excited by the longer-wavelength light 360 – 500 nm coming from the back of the electrodes. Given that enhancement of the SE IPCE in 300 – 360 nm was not significant, the photocurrents of R-1 – R-3 could not be promoted due to the very small portion of UV after AM 1.5 filter. In the case of R-3 under SE illumination, the enhancement of the IPCE in short wavelength could barely compensate the loss of that in wavelength longer than 360 nm, which overall presented as close photocurrent between R-0 and R-3.
Figure S9. The attenuation length as a function of wavelength for WO$_3$, regenerated from references 1$^5$ and 2$^6$. 
Figure S10. a, stability testing of the reduced WO$_3$ sample (R1). b, LSV for R1 before and after the stability testing. c, LSV for Reduction-200 s treatment on a WO$_3$ with a thickness of 1 μm.

Reference