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Supplementary Material

Promoting water photooxidation on transparent WO_3 thin films by an alumina overlayer

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1. Fig. S1-S5
2. Tables S1-S2

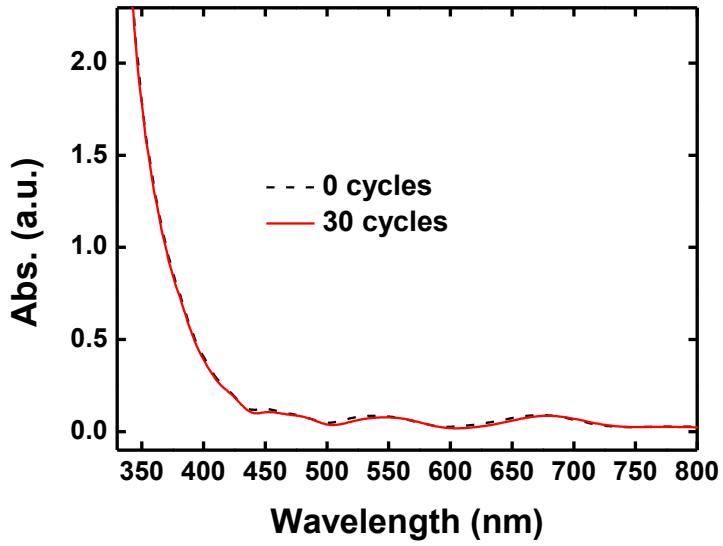

Fig. S1. Absorption spectra of transparent WO_3 and Al_2O_3/WO_3. The alumina overlayer was deposited by atomic layer deposition (ALD), for 0 cycles (black) or 30 cycles (red). At wavelengths larger than 440 nm, a typical interference pattern stemming from transparent thin film is observed.

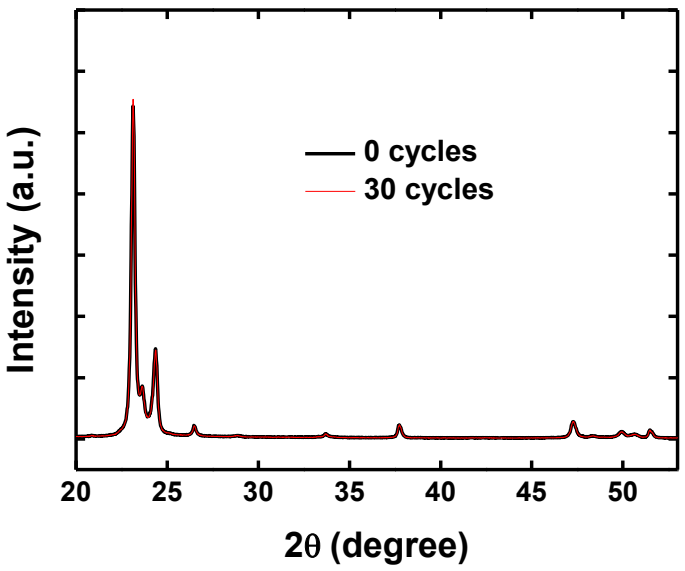

Fig. S2. XRD patterns of transparent WO_3 and Al_2O_3/WO_3. The alumina overlayer was deposited by atomic layer deposition (ALD), for 0 cycles (black) or 30 cycles (red).

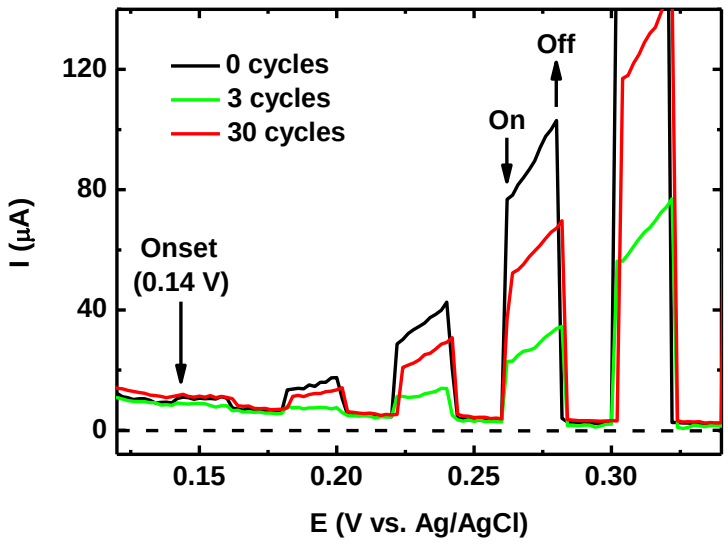

Fig. S3. Linear sweep voltammetry of transparent Al_2O_3/WO_3 electrodes, under chopped simulated AM 1.5G illumination. The alumina overlayer was deposited by atomic layer deposition (ALD), for 0 cycles (black), 3 cycles (green) or 30 cycles (red). Electrolyte: Ar-purged 0.1 M $HClO_4$. Scan rate: 2 mV/s.

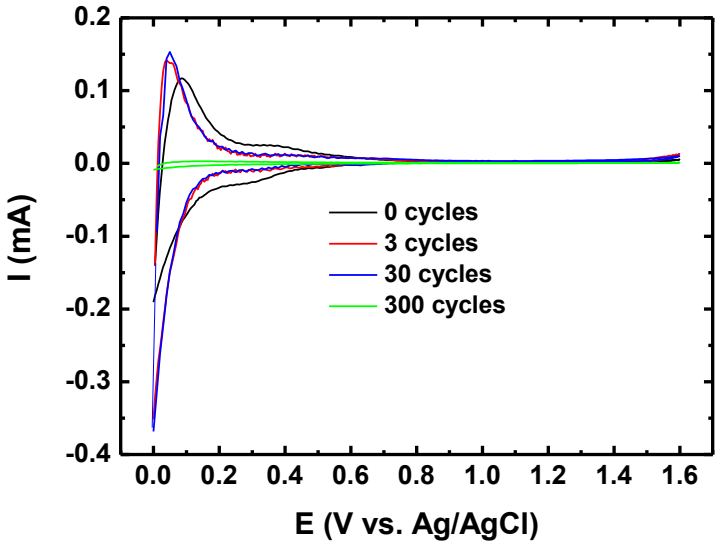

Fig. S4. Cyclic voltammetry of transparent Al_2O_3/WO_3 electrodes in the dark. The alumina overlayer was deposited by repeating the cycles of atomic layer deposition (ALD): 0 cycles (black), 3 cycles (red), 30 cycles (blue) or 300 cycles (green). Electrolyte: Ar-purged 0.1 M $HClO_4$. Scan rate: 20 mV/s.

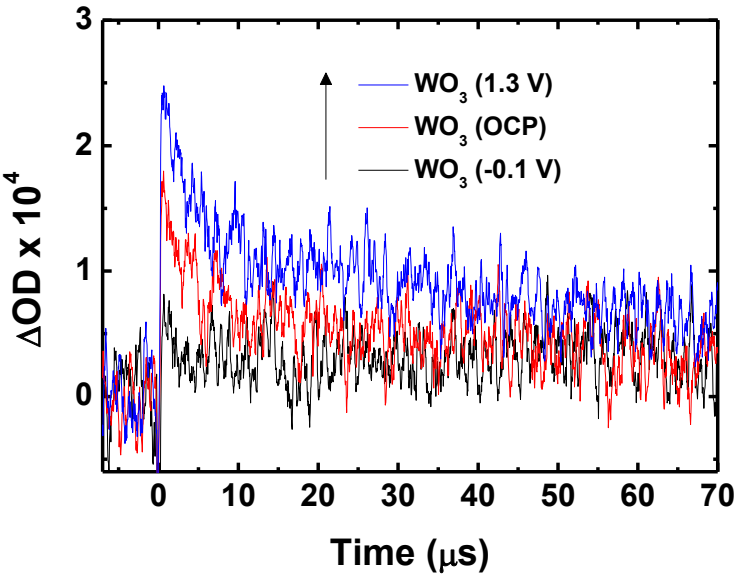

Fig. S5. Time traces observed at 480 nm during the 355-nm laser photolysis (250 μJ pulse^{-1}) of WO_3 in Ar-purged 0.1 M $HClO_4$ solution in the absence (open-circuit, OC) and presence of an applied bias (+1.3 V and –0.1 V vs. Ag/AgCl).

Table S1. Integrated photogenerated charge (Q_{ph}), evolved oxygen, and calculated faradaic efficiencies (η) obtained with WO_3 and Al_2O_3/WO_3 (30 ALD cycles) thin films.

Electrode	**Q_{ph} (C)**	**O_2 (μmol)**	**η(%)**
WO_3	6.245	2.868	17.7
Al_2O_3/WO_3	8.507	11.943	54.1

Table S2. Main parameters obtained upon fitting the deconvoluted TAS spectra (Fig. 7) with Gaussian functions. Peak positions (λ) and areas (A) are shown.

Electrode	**Trapped holes**		**Trapped electrons**	
	λ (nm)	A (au × nm)	λ (nm)	A (au × nm)
WO_3	455 ± 54	0.038 ± 0.054	611 ± 27	0.0104 ± 0.0183
Al_2O_3/WO_3	410 ± 148	0.108 ± 0.150	589 ± 88	0.0024 ± 0.0066