Electronic Supplementary Information for

Photoelectrochemical Oxidation of Anions by WO_3 in Aqueous and Nonaqueous Electrolytes

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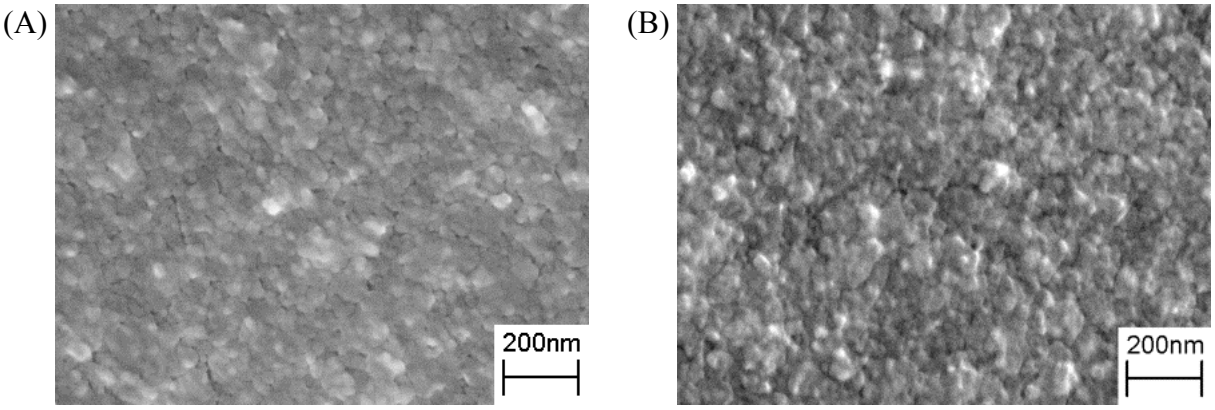

Fig. S1 Scanning electron micrographs of (A) WO_3/FTO and (B) WO_3/W photoanodes.

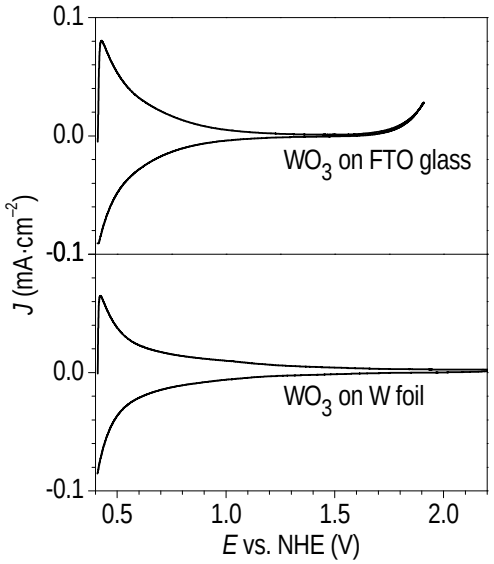

Fig. S2 Cyclic voltammograms for a WO_3/FTO electrode (top) and a WO_3/W electrode (bottom) in contact with 1.0 M HCl(aq) in the dark.

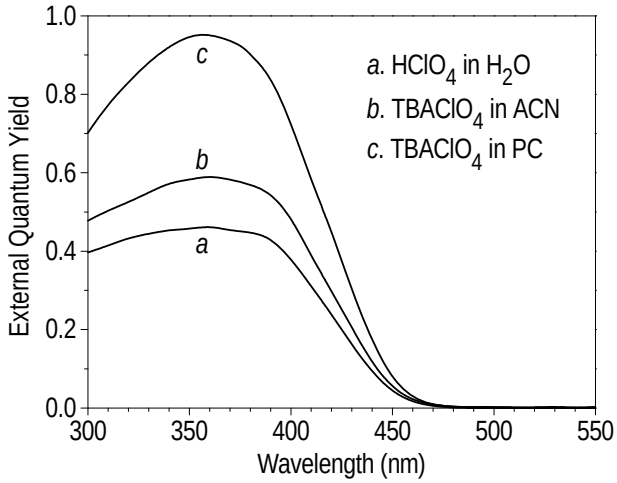

Fig. S3 External quantum yields (Φ_{ext}) of the WO_3/FTO photoanode in contact with electrolytes that contained ClO_4^-. During these measurements, the electrode potential was fixed in the plateau region in Fig. 1, i.e., 1.7 V vs. NHE for 1.0 M $HClO_4$ in water and 2.4 V for 0.50 M $TBAClO_4$ in ACN or PC.

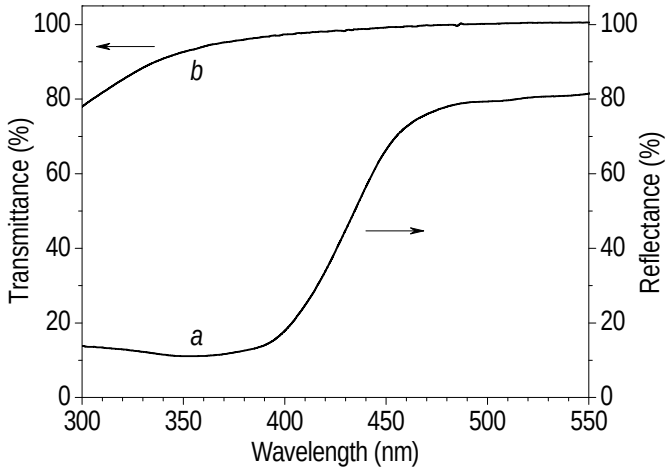

Fig. S4 Correction factors for calculating internal quantum efficiency (Φ_{int}) from external quantum efficiency (Φ_{ext}). (a) Diffuse reflectance spectrum of the WO_3/FTO photoanode. (b) Transmittance of propylene carbonate through a path length of 1.2 cm, which was calculated from the absorption spectrum of propylene carbonate measured against water. No light absorption was detectable in the shown wavelength range for the electrolytes in water or acetonitrile.

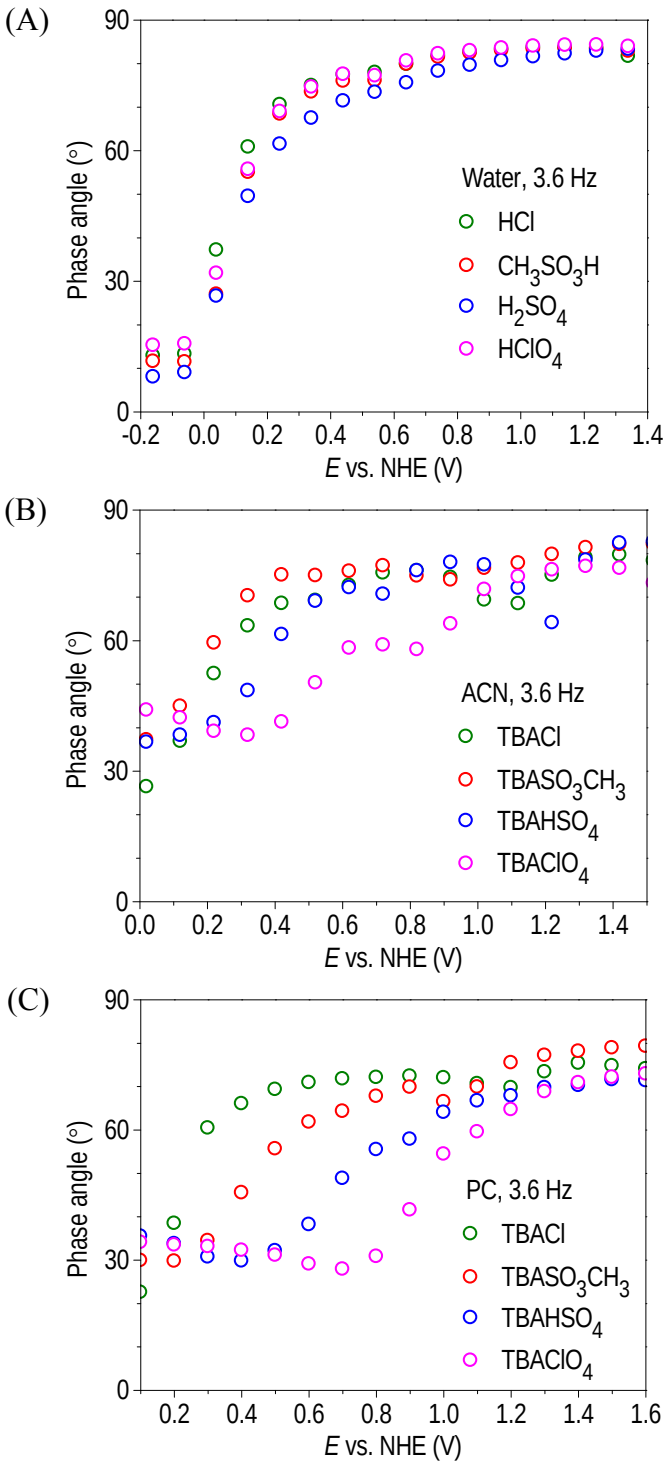

Fig. S5 Bode plots of electrochemical impedance data for a WO_3/FTO photoanode in contact with various electrolytes in (A) water, (B) acetonitrile, and (C) propylene carbonate. These data were also presented as the Mott–Schottky plots in Fig. 3.

Table S1 Flat-band potentials (E_{fb}, in V vs NHE) derived from linear fits in Fig. 3.

	Modulation frequency = 3.6 Hz				Modulation frequency = 36 Hz			
	Cl^-	$CH_3SO_3^-$	HSO_4^-	ClO_4^-	Cl^-	$CH_3SO_3^-$	HSO_4^-	ClO_4^-
Water	0.39	0.40	0.38	0.41	0.38	0.39	0.38	0.39
ACN	0.21	0.23	0.46	0.86	0.22	0.24	0.45	0.81
PC	0.22	0.44	0.70	0.96	0.21	0.44	0.68	0.92

Table S2 Dopant densities (N_D, in 10^{18} cm^{-3}) derived from linear fits in Fig. 3.

	Modulation frequency = 3.6 Hz				Modulation frequency = 36 Hz			
	Cl^-	$CH_3SO_3^-$	HSO_4^-	ClO_4^-	Cl^-	$CH_3SO_3^-$	HSO_4^-	ClO_4^-
Water	24	16	23	20	20	14	19	16
ACN	5.9	4.2	4.4	3.3	2.9	2.3	2.6	2.2
PC	1.1	1.8	2.6	3.7	0.5	0.8	1.2	2.2