PAPER

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The behavior of WO₃ photoanodes has been investigated in contact with a combination of four anions (Cl[−], CH₃SO₃[−], HSO₄[−], and ClO₄[−]) and three solvents (water, acetonitrile, and propylene carbonate), to elucidate the role of the semiconductor surface, the electrolyte, and redox kinetics on the current density vs. potential properties of n-type WO₃. In 1.0 M aqueous strong acids, although the flat-band potential (E_{fb}) of WO₃ was dominated by electrochemical intercalation of protons into WO₃, the nature of the electrolyte influenced the onset potential (E_{on}) of the anodic photocurrent. In aprotic solvents, the electrolyte anion shifted both E_{fb} and E_{on} , but did not significantly alter the overall profile of the voltammetric data. For 0.50 M tetra(*n*-butyl)ammonium perchlorate in propylene carbonate, the internal quantum yield exceeded unity at excitation wavelengths of 300–390 nm, indicative of current doubling. A regenerative photoelectrochemical cell based on the reversible redox couple B₁₀Br₁₀^{−/2−} in acetonitrile, with a solution potential of ~1.7 V vs. the normal hydrogen electrode, exhibited an open-circuit photovoltage of 1.32 V under 100 mW cm^{−2} of simulated Air Mass 1.5 global illumination.

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Broader context

Electrolytes are an indispensable constituent in (photo)electrochemistry for forming interfacial double layers and conducting currents. Nonetheless, it is generally considered that the role of electrolytes in (photo)electrochemistry is merely supporting and implicit, because the identity and concentration of electrolytes do not directly determine the electrode potentials and current densities. Results from this work suggest that when in contact with various aqueous and nonaqueous solutions and under simulated solar illumination, thin-film WO₃ photoanodes oxidized primarily the electrolyte anions in spite of the dominant molarity of the solvent in the electrolyte solutions. The priority of anion oxidation has been utilized to construct nonaqueous, regenerative photoelectrochemical cells that produce large open-circuit voltages. In addition to O₂(g) evolution from water, such electrolyte effects can result in undesired side reactions, and such processes should be taken into account when WO₃ photoanodes are incorporated into multi-component devices for solar-driven water splitting.

1 Introduction

WO₃ is an interesting photoanode material for use in early-generation tandem-type light absorber systems for solar-driven water splitting. In contact with aqueous solutions, photo-generated holes in the valence band of WO₃, at an electrochemical potential of ~3.0 V vs. the normal hydrogen electrode (NHE), are sufficiently oxidizing to produce free or surface-attached hydroxyl radicals (OH[•]) that can eventually lead to O₂(g). This widely accepted reaction scheme has inspired increasing interest^{1–10} in WO₃ photoanodes, both pristine and decorated with oxygen-evolving catalysts.

Several studies^{11–14} of the photoelectrochemical behavior of WO₃ in aqueous electrolytes have recently suggested that an

alternative process, in which oxidation of electrolyte anions, such as Cl[−], HSO₄[−], and ClO₄[−], effectively competes with oxidation of water at the WO₃/electrolyte interface, dominates the photoanodic behavior of n-type WO₃ especially under acidic conditions. Although some of the oxidation products (Cl₂ and S₂O₈^{2−}) have been confirmed experimentally,^{11–13} the importance of the oxidation of water to produce OH[•] as an energetic intermediate, relative to the oxidation of electrolyte anions, has yet to be fully elucidated.¹⁴ In aqueous media, the overwhelming molarity of water (>50 M) that hydrates and protonates the WO₃ surface makes disentangling these effects difficult. In contrast, valuable information can in principle be obtained by photoelectrochemical investigations of the same series of anions in nonaqueous electrolytes. Compared with main-group semiconductors such as Si¹⁵ and GaP,¹⁶ the photoelectrochemistry of metal oxides in nonaqueous solvents is not well elaborated. Early work regarding n-type TiO₂¹⁷ and ZnO¹⁸ electrodes in acetonitrile solutions placed emphasis on the behavior of the conduction-band electrons in these semiconductors.

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Nonaqueous electrolytes can also overcome the restriction on the available operational electrochemical potential window that is associated with operation in aqueous media. The flat-band potential (E_{fb}) of n-type WO_3 , at ~ 0.4 V vs. NHE,^{19,20} is too positive to effect the reduction of protons with no external bias applied to the system. Given the standard electrode potential for water oxidation, $E^0 = 1.23$ V vs. NHE, WO_3 photoanodes can therefore in theory generate an open-circuit voltage (V_{oc}) of at most ~ 0.8 V for water oxidation. Hence, much of the band gap energy of WO_3 ($E_g = 2.6$ eV)²¹ is not used electrochemically, and a substantial bias voltage from the photocathode is required to achieve overall water splitting. In nonaqueous electrolytes, existing knowledge about Si photoelectrodes^{22,23} predicts that both the E_{fb} of WO_3 and the Nernstian potential of the solution are tunable beyond these limits. To maximize the V_{oc} of regenerative photoelectrochemical cells, a nonaqueous redox system with a very positive Nernstian potential (e.g., >1.5 V vs. NHE) therefore needs to be identified.

We describe herein the nonaqueous photoelectrochemistry of WO_3 , and report the voltammetric, spectral response, and electrochemical impedance data obtained by using a combination of four anions (Cl^- , $CH_3SO_3^-$, HSO_4^- , and ClO_4^-) and three solvents (water, acetonitrile, and propylene carbonate). Furthermore, a regenerative photoelectrochemical cell has been constructed by use of a reversible redox couple, $B_{10}Br_{10}^{-/2-}$, that has a very positive formal reduction potential. The resulting WO_3 -based solid/liquid contact produced an open-circuit photovoltage of 1.32 V. Thus, the use of aprotic solvents and reversible redox couples aids in disentangling the contributions from the semiconductor surface, the electrolyte, and redox kinetics to the photoanodic behavior of WO_3 , and also opens a new venue for understanding other semiconducting metal oxides as photoanode materials.

II Experimental

Chemicals

Sodium tungstate dihydrate ($Na_2WO_4 \cdot 2H_2O$, Aldrich 223336, 99%), tungsten foil (Alfa Aesar 10417, 99.95%), 1.0 M hydrochloric acid (J. T. Baker 5620), acetonitrile (ACN, J. T. Baker 9035-10, ultra low water), propylene carbonate (PC, Aldrich 310328, anhydrous, 99.7%), tetra(*n*-butyl)ammonium chloride (TBACl, TCI America T0055, $>98\%$), tetra(*n*-butyl)ammonium bisulfate (TBAHSO₄, Aldrich 86868, $\geq 99\%$), and tetra(*n*-butyl)ammonium perchlorate (TBAClO₄, Fluka 86893, $\geq 99\%$) were used as received. Concentrated sulfuric acid (J. T. Baker 9681, 98%), methanesulfonic acid (Aldrich 471356, $\geq 99.5\%$), and perchloric acid (Fisher A2286, 60%) were diluted to 1.0 M using deionized water (18 M Ω cm resistivity) obtained from a Barnstead Nanopure system. All other chemicals were ACS reagents or were greater than 98% purity.

Tetra(*n*-butyl)ammonium methanesulfonate (TBASO₃CH₃, Fluka 86877, $\geq 97\%$) was recrystallized from toluene. Bis(methanesulfonyl) peroxide [$(CH_3SO_3)_2$] was synthesized²⁴ electrochemically as a white solid from a neat solution of sodium methanesulfonate in methanesulfonic acid. Bis[tetra(*n*-butyl)ammonium] decabromo-*closo*-decaborate(2-) ($TBA_2B_{10}Br_{10}$)

was prepared in two steps^{25,26} using decaborane (Alfa Aesar 87892, 98%), bromine, and tetra(*n*-butyl)ammonium bromide, and was subsequently recrystallized from acetone/ethanol as colorless needles. $TBA_2B_{10}Br_{10}$ is not hygroscopic and is readily soluble in aprotic organic solvents.

Electrochemistry

Electrochemical measurements were performed in a standard three-electrode configuration, in which a Pt-mesh counter electrode was isolated from the electrolyte by a medium glass frit, and the reference electrode was isolated from the electrolyte by a Luggin capillary. Voltammetric data were collected at a scan rate of 50 mV s⁻¹ using a BAS 100B electrochemical analyzer. The reference electrode for measurements in aqueous electrolytes was a Ag/AgCl/3.0 M NaCl electrode (Bioanalytical Systems, Inc.), which was taken to have a potential of $E = 0.209$ V vs. the normal hydrogen electrode (NHE). Nonaqueous reference electrodes were assembled from a AgCl-coated Ag wire, a filling solution, and a glass tube that had a Vycor frit at its tip.²⁷ The filling solution was saturated tetramethylammonium chloride (TMACl) in ACN, or saturated LiCl in PC.²⁸ The formal potential of the ferrocenium/ferrocene redox couple ($E^0(Fe^{+/0})$) vs. a nonaqueous reference electrode was measured by performing cyclic voltammetry and differential pulse voltammetry on a polished Pt-disc working electrode in 0.1 M TBAClO₄ in the corresponding solvent. Comparison with the known values²⁹ of $E^0(Fe^{+/0})$ vs. NHE in each solvent gave the potentials of these nonaqueous reference electrodes: $E(Ag/AgCl/sat. TMACl, ACN) = 0.06$ V vs. NHE, and $E(Ag/AgCl/sat. LiCl, PC) = 0.07$ V vs. NHE. All potentials measured in H₂O, ACN, or PC relative to the respective reference electrode were converted to values vs. NHE and the resulting potentials are reported herein.

WO_3 photoanodes

To form working electrodes, samples of SnO₂:F-coated glass slides (FTO, Hartford Glass, TEC 15) and W foil were cut into pieces that were 1.0 cm in width. After immersing the slides for 30 min in a modified piranha solution (1.0 g (NH₄)₂S₂O₈ in 20 mL concentrated H₂SO₄), the substrates were rinsed with H₂O and then with ethanol, to create a clean, hydrophilic surface that adhered well to the WO_3 overlayer. A column (Sigma C4169, $\varnothing 1.5$ cm $\times$ 10 cm) packed with strongly acidic ion-exchange resin (Fisher Rexyn 101 (H), 1.9 mEq. mL⁻¹) was washed with deionized water until the pH value of the washings was ~ 4 . The column was then loaded with 0.566 mL (0.5 mmol) of 3% H₂O₂ and a solution of 0.330 g (1.00 mmol) $Na_2WO_4 \cdot 2H_2O$ in 1.50 mL water, and was subsequently eluted with 20 mL of deionized water. The eluate was a clear, pale yellow solution of peroxytungstic acid, and was immediately consumed in the next step. Peroxide test strips (EM Quant 10081-1) indicated that the free H₂O₂ concentration was 10–30 ppm in this solution.

A cleaned electrode substrate (FTO glass or W foil) was electrically connected to a Cu clamp, and was immersed in the peroxytungstic acid to a depth of 1.0 cm. The cathodic electro-deposition of WO_3 was performed, without stirring, at -0.29 V

vs. NHE, with the passage of -0.25 C cm^{-2} of charge density (at a current density of $\sim -0.4 \text{ mA cm}^{-2}$) yielding a blue layer of reduced $\text{WO}_3 \cdot x\text{H}_2\text{O}$ on the working electrode surface, as well as O_2 bubbles at the Pt counter electrode. The working electrode was removed from the bath, rinsed with water, dried in air, and baked at 225°C until the blue color had faded completely, typically requiring ~ 10 min of baking time. The deposition-dehydration cycle was then repeated. After 5–6 cycles, the electrode was annealed at 500°C in air for 1 h, yielding a pale yellow film of WO_3 . The mass and thickness of the electrodeposited WO_3 film were determined using a Sartorius CPA225D semi-micro balance and a Dektak XT profilometer, respectively. Unsealed with epoxy, WO_3/FTO electrodes were heated at 225°C for 10 min before each new experiment. The WO_3/W electrode was electrically connected to a Cu wire, and was sealed with epoxy resin (Loctite Hysol 9460) completely on one side and partially on the other side to expose $\sim 1.0 \text{ cm}^2$ of WO_3 but no bare W.

Photoelectrochemistry

Voltammetric current density vs. potential (J - E) data (50 mV s^{-1}) were collected using a BAS 100B electrochemical analyzer and a solar simulator, in conjunction with a photoelectrochemical cell that has been described previously.¹² Illumination was provided by an Oriol solar simulator equipped with an Air Mass 1.5 global (AM 1.5G) filter. The light intensity was adjusted at the sample plane to provide the same open-circuit voltage on a secondary standard (a Solarex Si photodiode) as that produced by illumination of the photodiode with 100 mW cm^{-2} of AM 1.5G illumination. The electrolyte produced a 1.2 cm optical path length between the optical window and the working electrode. A miniature cell was fabricated similarly from a 10 mL round bottom flask, whose single neck provided access for all of the electrodes. The error in the values of the photocurrent density (J) was estimated to be $\pm 10\%$.

Spectral response measurements were performed using ultraviolet and visible light produced by a 150 W Xe arc lamp. The light was chopped at 1.0 Hz , and was passed through a monochromator that had slits 0.5 mm in width. Either the photoelectrochemical cell or a calibrated Si photodiode (OSI Optoelectronics, UV-50) was positioned in the light path, and the illuminated spot was focused to $\sim 1 \times 1 \text{ mm}^2$ at the front surface of the working electrode. At a fixed potential, the wavelength of the incident light was varied in 10 nm steps, and the resulting photocurrents were measured with lock-in detection using a Gamry Series G 300 potentiostat. The external quantum yield (Φ_{ext}) of the photoelectrochemical cell was calculated based on the known Φ_{ext} values of the calibrated Si diode. To compensate for fluctuations in the intensity of the monochromatic illumination, a small fraction of the light beam was split using a quartz plate and was continuously monitored by another Si photodiode.

Electrochemical impedance spectroscopy (EIS)

EIS was performed in the absence of illumination on a PARSTAT 2273 potentiostat/frequency response analyzer using the

PowerSUITE software. To allow for equilibration between the WO_3 film and the nonaqueous electrolytes, prior to each impedance measurement five voltammetric cycles were run under illumination over the same potential range as used for collecting the impedance data. For each modulation frequency between 20 mHz and 2.0 MHz (four frequency values per decade), the reactance of a WO_3/FTO electrode was measured over a potential range of 1.6 V in the aqueous electrolytes and of 2.3 V in the nonaqueous electrolytes, in parallel with the potential ranges of the corresponding voltammetric scans. The EIS dataset thus obtained was fitted using MATLAB to produce Mott-Schottky plots and additionally to extract E_{fb} values from the resulting data.

Spectrophotometry and microscopy

The absorption spectra of electrolytes were measured in a 1 cm quartz cuvette using an Agilent 8453 UV-visible spectrophotometer. The diffuse reflectance spectrum of the WO_3/FTO photoanode was taken on a Cary 5000 UV-visible spectrophotometer by placing the photoanode in the center of an integrating sphere. Field-emission scanning electron microscopy (FESEM) was performed on a Zeiss model 1550VP.

III Results

WO_3/FTO and WO_3/W photoanodes

WO_3 films on FTO-coated glass or W foil were fabricated by cathodic electrodeposition from peroxytungstic acid and subsequent annealing in air. Fig. S1 (ESI[†]) shows that these two types of WO_3 films possessed similar surface morphology with crystallites $\sim 50 \text{ nm}$ in size and crevices between the crystallites. The porosity of the WO_3 films that were electrodeposited on FTO-coated glass was calculated to be 22% , based on the measured dimension ($1.6 \pm 0.1 \mu\text{m} \times 1.0 \text{ cm}^2$) and mass ($0.90 \pm 0.02 \text{ mg}$) of the WO_3 films, in addition to the density (7.2 g cm^{-3}) of crystalline WO_3 .¹³ During annealing, the surface of the W foil developed a thin oxide layer so the mass of the electrodeposited WO_3 on W could not be directly determined by the mass gain of the W substrate. Fig. S2 (ESI[†]) shows the cyclic voltammetric data acquired from these electrodes in 1.0 M HCl(aq) under room light, referred to as “dark”. For the WO_3/FTO electrode, the anodic current showed an onset at $E = \sim 1.6 \text{ V}$ vs. NHE. The current density was largely uniform across the film area, as probed using a pipette that was filled with 1.0 M HCl(aq) and that contacted $\sim 0.01 \text{ cm}^2$ of the WO_3 surface. For the WO_3/W electrode, the anodic current originated only from the edges of the W foil. After sealing the back and edges of the electrode with epoxy resin, no significant faradaic current was observed in the dark at $E = 0.6\text{--}2.2 \text{ V}$ vs. NHE.

Photoelectrochemical oxidation of anions

Photoelectrochemical experiments were performed on a WO_3/FTO electrode in one of three different solvents (water, ACN, and PC) that each contained one of four anions (Cl^- , CH_3SO_3^- , HSO_4^- , and ClO_4^-). Fig. 1 displays the J - E characteristics of a WO_3/FTO electrode in contact with these electrolytes, with the

Fig. 1 Voltammograms of a WO_3/FTO photoanode in (A) water, (B) ACN, and (C) PC that contained Cl^- (green), CH_3SO_3^- (red), HSO_4^- (blue), or ClO_4^- (magenta), under simulated sunlight (AM 1.5G illumination, 100 mW cm^{-2}). The electrolytes were 1.0 M acids in water and 0.50 M tetra(*n*-butyl)ammonium salts in ACN or PC. All panels also depict the results from control experiments with HSO_4^- in the dark (black).

aqueous electrolytes containing 1.0 M acid and the nonaqueous ACN or PC electrolytes containing 0.50 M of the appropriate tetra(*n*-butyl)ammonium salt. The dark current densities were $<0.05 \text{ mA cm}^{-2}$ at $E = 0.6\text{--}1.9 \text{ V vs. NHE}$. In contact with the aqueous acids, capacitive current densities were observed in the dark for $E < 0.6 \text{ V vs. NHE}$. The WO_3 film turned blue at $E < 0.2 \text{ V vs. NHE}$, and fragmented and delaminated at more negative potentials. In ACN or PC, no color change of WO_3 was observed at $E = -0.1 \text{ V vs. NHE}$.

The onset potential of the photocurrent (E_{on}) was a function of the electrolyte anion, following the order $E_{\text{on}}(\text{Cl}^-) < E_{\text{on}}(\text{CH}_3\text{SO}_3^-) < E_{\text{on}}(\text{HSO}_4^-) < E_{\text{on}}(\text{ClO}_4^-)$. The photocurrent densities rose steadily for $E > E_{\text{on}}$, and in water and ACN eventually reached a plateau value (J_{ph}) that was insensitive to the electrolyte. In PC, however, the J_{ph} value increased from 1.5 mA cm^{-2} for

the TBACl electrolyte to 2.3 mA cm^{-2} for TBAClO_4 , and exhibited intermediate values for the other electrolytes. When passing a photocurrent density of J_{ph} , the WO_3 surfaces exhibited no observable gas bubbles or color change. At the Pt counter electrode, a gas, presumably H_2 from the following cathode reactions, was evolved from electrolytes containing TBAHSO_4 or PC:

For TBACl, $\text{TBASO}_3\text{CH}_3$, or TBAClO_4 in ACN, the electrolyte in the cathode chamber turned yellow, which could be due to a reductive condensation reaction involving acetonitrile. The J - E behavior of the WO_3/W photoanode resembled that of the WO_3/FTO photoanode, but the former produced $\sim 10\%$ less photocurrent density than the latter under the same conditions.

Spectral response

The external quantum yield (Φ_{ext}) of the WO_3/FTO photoanode was measured at fixed electrode potentials in the plateau region of the J - E data shown in Fig. 1. For example, Fig. S3 (ESI†) shows the results obtained at 1.7 V vs. NHE for 1.0 M HClO_4 in water, and at 2.4 V vs. NHE for 0.50 M TBAClO_4 in ACN or PC. The diffuse reflectance data for the WO_3/FTO photoanode ($R_{\text{electrode}}$) and the transmittance of the electrolyte between the light source and the WO_3 ($T_{\text{electrolyte}}$), both presented in Fig. S4 (ESI†), were used to convert the Φ_{ext} values to internal quantum yields (Φ_{int}):

$$\Phi_{\text{int}} = \Phi_{\text{ext}}/T_{\text{electrolyte}}/(1 - R_{\text{electrode}}) \quad (1)$$

For the electrolytes in water or ACN, the values of $T_{\text{electrolyte}}$ were essentially unity at wavelengths $\geq 300 \text{ nm}$. Fig. 2 shows a plot of Φ_{int} vs. wavelength for the WO_3/FTO photoanode in contact with electrolytes that contained ClO_4^- . The spectral response displayed similar profiles for all three solvents, with Φ_{int} maximizing at 350–360 nm and approaching zero at $\geq 480 \text{ nm}$, the latter coincident with the optical band gap of WO_3 at 2.6 eV.²¹ However, the solvent had an impact on the magnitude of Φ_{int} , which at 300–390 nm exceeded unity in PC, but was only ~ 0.5 in

Fig. 2 Internal quantum yields (Φ_{int}) calculated according to eqn (1), for a WO_3/FTO photoanode in contact with electrolytes that contained ClO_4^- .

Table 1 Maximum values of the internal quantum yield (Φ_{int}) of a WO_3/FTO photoanode in contact with various solvents and electrolytes, under the same conditions as in Fig. 1

	Cl^-	CH_3SO_3^-	HSO_4^-	ClO_4^-
Water	0.57	0.56	0.55	0.53
ACN	0.63	0.65	0.63	0.66
PC	0.69	0.79	0.87	1.15

water. Table 1 summarizes the maxima of Φ_{int} for WO_3 in all solvent–electrolyte combinations investigated in this work.

Electrochemical impedance spectroscopy

Fig. S5 (ESI†) shows representative Bode plots of the EIS data for a polycrystalline WO_3/FTO photoanode in contact with various electrolyte–solvent combinations. In the frequency range of ~ 1

to 50 Hz, the measured impedance data were in the capacitive regime, and the differential capacitance (C) was extracted at each potential (E) of the WO_3/FTO photoanode. Fig. 3 presents Mott–Schottky plots of C^{-2} vs. E , and Tables S1 and S2† list the values of E_{fb} and of the dopant density (N_{D}), respectively, obtained by the linear fits depicted in Fig. 3. In 1.0 M aqueous strong acids, these plots (Fig. 3A) displayed little dependence on the electrolyte anion at frequencies from 0.3 Hz to at least 0.3 kHz. In contrast, the Mott–Schottky plots for WO_3 in ACN (Fig. 3B) or in PC (Fig. 3C) were strongly affected by the electrolyte anion. The relative order of the E_{fb} values with different electrolytes, from more negative to more positive, was $E_{\text{fb}}(\text{Cl}^-) \approx E_{\text{fb}}(\text{CH}_3\text{SO}_3^-) < E_{\text{fb}}(\text{HSO}_4^-) < E_{\text{fb}}(\text{ClO}_4^-)$ in ACN and similarly was $E_{\text{fb}}(\text{Cl}^-) < E_{\text{fb}}(\text{CH}_3\text{SO}_3^-) < E_{\text{fb}}(\text{HSO}_4^-) < E_{\text{fb}}(\text{ClO}_4^-)$ in PC. These relationships were conserved for results obtained over a three decade range of frequencies, and were reproduced by two independent sets of measurements.

Regenerative photoelectrochemistry

The $\text{B}_{10}\text{Br}_{10}^{-1/2-}$ redox couple was produced by mixing decabromo-*closo*-decaborate ($\text{B}_{10}\text{Br}_{10}^{2-}$) and bis(methanesulfonyl) peroxide $[(\text{CH}_3\text{SO}_3)_2]$ in dry, air-saturated ACN. Fig. 4 shows the UV-visible absorption spectrum of $\text{B}_{10}\text{Br}_{10}^{-1/2-}$, whose black-brown color³¹ appeared within minutes of the reaction, and subsequently persisted for several weeks. In contact with the

Fig. 3 Mott–Schottky plots of the differential capacitance (C) vs. potential (E) of a WO_3/FTO photoanode in (A) water, (B) ACN, and (C) PC that contained Cl^- (green), CH_3SO_3^- (red), HSO_4^- (blue), or ClO_4^- (magenta), each measured at two modulation frequencies in the dark immediately after five corresponding J – E scans in Fig. 1 were performed. Other conditions were identical to those in Fig. 1. Values of flat-band potential (E_{fb}) were estimated by linear extrapolation (solid lines) of the experimental data (open circles).

Fig. 4 UV-visible spectrum of the radical anion $\text{B}_{10}\text{Br}_{10}^{-1/2-}$, generated in ACN by oxidizing $\text{B}_{10}\text{Br}_{10}^{2-}$ with $(\text{CH}_3\text{SO}_3)_2$. The calculated absorbance values are approximate. Inset: a ball-and-stick model of $\text{B}_{10}\text{Br}_{10}^{-1/2-}$, where the pink balls stand for B and the brown balls for Br.

Fig. 5 Voltammograms of a WO_3/W photoanode in contact with 1 mM $\text{B}_{10}\text{Br}_{10}^{-1/2-}$ and 0.50 M $\text{TBASO}_3\text{CH}_3$ in ACN, in the dark (black) or under 100 mW cm^{-2} of AM 1.5G illumination (red). These J – E data were referenced to NHE, as well as to a Pt wire that probed $E(\text{B}_{10}\text{Br}_{10}^{-1/2-})$ as the solution potential.

$\text{B}_{10}\text{Br}_{10}^{-/2-}$ redox couple in ACN, the WO_3/FTO photoanode generated negligible photocurrent density. No damage to the WO_3 film was observable, and the J - E behavior of the WO_3/FTO photoanode fully recovered when the photoanode was rinsed with acetone and tested in an electrolyte that did not contain any deliberately added $\text{B}_{10}\text{Br}_{10}^{-/2-}$. In contrast, Fig. 5 shows the photoelectrochemical performance of the WO_3/W photoanode in contact with 1 mM $\text{B}_{10}\text{Br}_{10}^{-/2-}$ and 0.50 M $\text{TBASO}_3\text{CH}_3$ in ACN, whose solution potential was determined by a Pt wire to be 1.68 V vs. NHE. In the dark, the WO_3/W photoanode produced very small ($<0.05 \text{ mA cm}^{-2}$) anodic current densities, but exhibited significant cathodic current densities at potentials $<\sim 0.4 \text{ V}$ vs. NHE. Under 100 mW cm^{-2} of simulated AM 1.5G illumination, the cell produced a short-circuit photocurrent density, $J_{\text{sc}} = 1.06 \text{ mA cm}^{-2}$, an open-circuit voltage, $V_{\text{oc}} = 1.32 \text{ V}$, a fill factor of 0.50, and a photoelectrode energy-conversion efficiency of $\eta = 0.71\%$ (which included losses due to light extinction by $\text{B}_{10}\text{Br}_{10}^{-}$ and to solution resistances).

IV Discussion

Porous WO_3 photoanodes

WO_3 photoanodes have been fabricated by electrodeposition from peroxytungstic acid, and have been characterized by X-ray diffraction and scanning electron microscopy.^{12,13,32} In previous preparations of peroxytungstic acid, W metal was reacted with concentrated $\text{H}_2\text{O}_2(\text{aq})$ and then the excess H_2O_2 was decomposed. However, in the peroxytungstic acid thus obtained, the concentration of the residual free H_2O_2 , which has been found¹² to be critical for the electrodeposition, is difficult to reproduce precisely. In this work, peroxytungstic acid was prepared within minutes by proton exchange of $\text{Na}_2\text{WO}_4(\text{aq})$ in the presence of a stoichiometric amount of H_2O_2 , and the peroxytungstic acid was consumed promptly in the subsequent electrodeposition. This procedure provided excellent reproducibility in the resulting peroxytungstic acid, as well as in the photoelectrochemical performance of the WO_3 photoanodes.

The (photo)electrochemical experiments described herein suggest that the WO_3 films, prepared by electrodeposition and annealing, were porous across the entire film thickness. For the WO_3/FTO photoanode, the electrolyte percolated into the WO_3 film and contacted the conducting FTO substrate. Thus the WO_3/FTO photoanode oxidized 1.0 M $\text{HCl}(\text{aq})$ in the dark at $E \sim 1.6 \text{ V}$ vs. NHE, a potential in the band gap region of WO_3 . Nevertheless, the WO_3/FTO photoanode produced substantial photocurrent densities in contact with 1.0 M $\text{HCl}(\text{aq})$, because the Cl^-/Cl_2 redox couple could not be rapidly regenerated by electrons in the FTO substrate. In contrast, when contacted with the electrochemically reversible $\text{B}_{10}\text{Br}_{10}^{-/2-}$ redox couple, the WO_3/FTO photoanode produced a nearly complete loss of photocurrent, which can be explained by severe current shunting at the FTO/electrolyte interface. The minimal current shunting observed for the same electrolyte and redox couple conditions for the WO_3/W electrode is consistent with expectations for the presence of a compact oxide layer on the W surfaces that prevented direct contact between the W and the Cl^- or $\text{B}_{10}\text{Br}_{10}^{-}$ in the electrolyte.

Proton intercalation of WO_3 in aqueous acids

The capacitive dark currents (Fig. S2†) and electrochromism of the WO_3 photoanodes in aqueous acids are consistent with the electrochemical intercalation of protons into WO_3 as per eqn (2):

This reaction has a standard electrode potential of 0.29 V vs. NHE for $x = 1$.³³ The formation of H_xWO_3 is consistent with the blue color observed for the cathodically charged WO_3 films, and for the internal stress that accumulated within the WO_3 film at large negative potentials.

Eqn (2) also provides a consistent explanation for the differential capacitance data in Fig. 3A and other data reported previously,³⁴ which indicate that the E_{fb} value for WO_3 in contact with a variety of 1.0 M aqueous strong acids was nearly independent of the electrolyte. At $E \leq 0.4 \text{ V}$ vs. NHE, H_xWO_3 with x calculated to be >0.1 is degenerately doped and thus not photoactive. For $E = 0.4$ – 1.2 V vs. NHE, the J - E data in Fig. 1A exhibited values of E_{on} that were a function of the anion. In aqueous strong acids, WO_3 photoanodes have been shown to preferentially oxidize the acid anions relative to the oxidation of water.^{11–13} The anion-dependent E_{on} values have therefore been suggested to reflect a competition between the different rates of charge recombination and of interfacial electron transfer in each system.³⁵ In this framework, $\text{Cl}^-(\text{aq})$ would have the highest ratio of charge transfer relative to recombination, and therefore produces significant photocurrent densities at the most negative E_{on} value of all of the anions studied herein.

WO_3 /electrolyte interfaces in aprotic solvents

In ACN or PC, electrochromism of the WO_3 film was not observed. The J - E data of Fig. 1B and C indicate that in these solvents, the differences between the onset and inflection potentials were almost constant, with a value of $\sim 0.7 \text{ V}$. Photoelectrochemical oxidation of the electrolyte anions presumably involves radical intermediates ($\text{Cl}^\cdot$, $\text{CH}_3\text{SO}_3^\cdot$, $\text{HSO}_4^\cdot$, and $\text{ClO}_4^\cdot$) that are adsorbed to the WO_3 surface *via* a labile O–Cl or O–O bond, prior to the formation of more stable oxidation products such as $\text{Cl}_2(\text{g})$, $(\text{CH}_3\text{SO}_3)_2$, and $\text{S}_2\text{O}_8^{2-}$ (the final oxidation product of $\text{ClO}_4^\cdot$ was unidentified). The surface potential of the WO_3 photoanode can therefore be significantly influenced in aprotic solvents by the adsorbed radical species, in which interfacial electric dipoles with partial positive charges on the electrolyte side and partial negative charges on the WO_3 side can offset a portion of the applied anodic potential. This mechanistic picture is strongly supported by the systematic shift in E_{fb} for WO_3 in contact with the various electrolytes (Fig. 3B and C), and also agrees with current knowledge of the surface modification of Si photoelectrodes.²³

The presence of surface-attached radicals is also consistent with the values of J_{ph} and Φ_{int} observed for WO_3 photoanodes in contact with 0.50 M TBAClO_4 in PC. Φ_{int} values exceeding unity indicate that more than one conduction-band electron was

generated by an absorbed photon. Current doubling takes place when an electrode reaction involves reactive intermediates, usually free radicals, that inject majority carriers (*i.e.*, electrons for an n-type photoanode and holes for a p-type photocathode) into the electrode, in addition to photogenerated carriers.^{4,36} One explanation of the data is that the radical intermediate $\text{ClO}_4^\cdot$ was not reducing enough to cause current doubling in water and ACN, but could oxidize an adjacent PC molecule to a PC radical:

A similar reaction between PC and the hydroxyl radical is known,³⁷ and the standard reduction potential of $\text{OH}^\cdot$ (2.85 V)³⁸ is close to that of $\text{ClO}_4^\cdot$ (2.75 V *vs.* NHE);³⁹ many other organic oxygenates have also been shown^{4,40} to be responsible for current doubling. The newly formed PC radical would then be able to inject an electron to the conduction band of WO_3 before diffusing away from the electrode surface, leading to $\Phi_{\text{int}} > 1$. The values of Φ_{int} shown in Table 1 for other electrolytes (0.50 M Cl^- , CH_3SO_3^- , or HSO_4^- in PC) are well below unity, which is consistent with the expectation that their radical forms ($\text{Cl}^\cdot$, $\text{CH}_3\text{SO}_3^\cdot$, or $\text{HSO}_4^\cdot$) are more subject to dimerization than to reaction with PC, thereby terminating current doubling. These results clearly demonstrate that at the WO_3 /electrolyte interface, discharging of the electrode anion is the predominant process, whereas oxidation of the solvent is only a secondary reaction.

Regeneration of photoanodic products

In aqueous acids, E_{on} is limited by proton intercalation in WO_3 , and the photoanodic product is ultimately $\text{O}_2(\text{g})$. Compared with water, ACN possesses a much wider potential window, and allows for more negative values of E_{on} for WO_3 in contact with Cl^- , CH_3SO_3^- , or HSO_4^- (Fig. 1A and B). The photoanodic products of the latter two anions are powerful oxidants: $E^0(\text{HSO}_4^-/\text{S}_2\text{O}_8^{2-}) = 2.12$ V *vs.* NHE,³⁸ whereas the value of $E^0(\text{CH}_3\text{SO}_3^-/(\text{CH}_3\text{SO}_3)_2)$ has so far been unreported but is predicted to be < 2.12 V. However, these two-electron redox couples are not reduced at a reasonable overpotential on Pt surfaces. For example, the cathodic reduction of $\text{S}_2\text{O}_8^{2-}(\text{aq})$ is reported⁴¹ to occur at ~ 0.6 V *vs.* NHE, a potential much more negative than $E^0(\text{HSO}_4^-/\text{S}_2\text{O}_8^{2-})$.

In this work, $(\text{CH}_3\text{SO}_3)_2$ was activated by decabromo-*closo*-decaborate ($\text{B}_{10}\text{Br}_{10}^{2-}$), a spheroid-shaped anion that is depicted in the inset of Fig. 4:

$\text{B}_{10}\text{Br}_{10}^{2-}$ exhibits high chemical stability²⁶ and a reversible, one-electron redox system with a formal oxidation potential of 1.78 V *vs.* NHE.³¹ The Nernst potential of the solution as probed by a Pt wire was observed to be 1.68 V *vs.* NHE, therefore providing an opportunity to produce large barrier heights, and correspondingly large open-circuit voltages from regenerative photoelectrochemical cells that use this redox system in contact with WO_3 photoanodes.

When 1 mM $\text{B}_{10}\text{Br}_{10}^{-/2-}$ was introduced to 0.50 M $\text{TBA-SO}_3\text{CH}_3$ in ACN, the WO_3/W photoanode exhibited $E_{\text{oc}} = 0.36$ V *vs.* NHE, corresponding to an open-circuit voltage (V_{oc}) of 1.32 V. This value is by far in excess of the nominal V_{oc} that WO_3 can generate in aqueous electrolytes (≤ 0.8 V). Thus, the $\text{B}_{10}\text{Br}_{10}^{-/2-}$ redox system provided an approach to convert the chemical energy that was stored in $(\text{CH}_3\text{SO}_3)_2$ into a solution potential that could readily generate electrical power, at the expense of a loss in potential of 0.2–0.3 V. A drawback to the use of this redox couple is that the oxidized species, $\text{B}_{10}\text{Br}_{10}^-$, absorbed a portion of the incoming light, and contributed to a reduction of J_{ph} from ~ 1.4 mA cm^{-2} in Fig. 1B to 1.06 mA cm^{-2} (in Fig. 5). Such optical losses can be minimized in cell configurations that utilize a thin layer of electrolyte,⁴² and/or deeply integrated electrolyte/electrode microstructures.⁴³

V Conclusions

In contact with 1.0 M aqueous strong acids, at $E = 0.4$ –1.2 V *vs.* NHE, charge recombination competed with anion oxidation at the WO_3 /electrolyte interfaces, leading to an anion-dependent onset of photoanodic current, although the flat-band potential stayed nearly constant. In aprotic solvents, both the flat-band potential and the onset potential of the photoanodic current shifted as the anion was changed, but the overall profile of the J – E data remained relatively constant. WO_3 photoanodes in contact with 0.50 M TBAClO_4 in PC exhibited Φ_{int} values greater than unity at 300–390 nm, owing to current doubling. When WO_3 was used as a photoanode in a regenerative photoelectrochemical cell configuration, the reversible, high-potential redox system 1 mM $\text{B}_{10}\text{Br}_{10}^{-/2-}$ with 0.50 M $\text{TBASO}_3\text{CH}_3$ in ACN produced a solution potential of ~ 1.7 V *vs.* NHE, and an open-circuit voltage of 1.32 V under 100 mW cm^{-2} of simulated AM 1.5G illumination.

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References

- 1 G. Hodes, D. Cahen and J. Manassen, *Nature*, 1976, **260**, 312–313.
- 2 W. Erbs, J. Desilvestro, E. Borgarello and M. Grätzel, *J. Phys. Chem.*, 1984, **88**, 4001–4006.
- 3 K. Sayama, R. Yoshida, H. Kusama, K. Okabe, Y. Abe and H. Arakawa, *Chem. Phys. Lett.*, 1997, **277**, 387–391.
- 4 C. Santato, M. Ulmann and J. Augustynski, *J. Phys. Chem. B*, 2001, **105**, 936–940.
- 5 A. Valdes and G. J. Kroes, *J. Chem. Phys.*, 2009, **130**, 114701.

- 6 R. Liu, Y. J. Lin, L. Y. Chou, S. W. Sheehan, W. S. He, F. Zhang, H. J. M. Hou and D. W. Wang, *Angew. Chem., Int. Ed.*, 2011, **50**, 499–502.
- 7 F. M. Pesci, A. J. Cowan, B. D. Alexander, J. R. Durrant and D. R. Klug, *J. Phys. Chem. Lett.*, 2011, **2**, 1900–1903.
- 8 J. Brillet, J. H. Yum, M. Cornuz, T. Hisatomi, R. Solarska, J. Augustynski, M. Grätzel and K. Sivula, *Nat. Photonics*, 2012, **6**, 823–827.
- 9 X. Liu, F. Y. Wang and Q. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 7894–7911.
- 10 S. S. K. Ma, K. Maeda, R. Abe and K. Domen, *Energy Environ. Sci.*, 2012, **5**, 8390–8397.
- 11 J. Augustynski, R. Solarska, H. Hagemann and C. Santato, *Proc. SPIE*, 2006, **6340**, 63400J.
- 12 Q. X. Mi, A. Zhanaidarova, B. S. Brunschwig, H. B. Gray and N. S. Lewis, *Energy Environ. Sci.*, 2012, **5**, 5694–5700.
- 13 J. C. Hill and K. S. Choi, *J. Phys. Chem. C*, 2012, **116**, 7612–7620.
- 14 R. Solarska, R. Jurczakowski and J. Augustynski, *Nanoscale*, 2012, **4**, 1553–1556.
- 15 E. A. Santori, J. R. Maiolo, M. J. Bierman, N. C. Strandwitz, M. D. Kelzenberg, B. S. Brunschwig, H. A. Atwater and N. S. Lewis, *Energy Environ. Sci.*, 2012, **5**, 6867–6871.
- 16 N. C. Strandwitz, D. B. Turner-Evans, A. C. Tamboli, C. T. Chen, H. A. Atwater and N. S. Lewis, *Adv. Energy Mater.*, 2012, **2**, 1109–1116.
- 17 S. N. Frank and A. J. Bard, *J. Am. Chem. Soc.*, 1975, **97**, 7427–7433.
- 18 P. A. Kohl and A. J. Bard, *J. Am. Chem. Soc.*, 1977, **99**, 7531–7539.
- 19 D. E. Scaife, *Sol. Energy*, 1980, **25**, 41–54.
- 20 M. T. Nenadovic, T. Rajh, O. I. Micic and A. J. Nozik, *J. Phys. Chem.*, 1984, **88**, 5827–5830.
- 21 F. P. Koffyberg, K. Dwight and A. Wold, *Solid State Commun.*, 1979, **30**, 433–437.
- 22 N. S. Lewis, *J. Electrochem. Soc.*, 1984, **131**, 2496–2503.
- 23 R. L. Grimm, M. J. Bierman, L. E. O'Leary, N. C. Strandwitz, B. S. Brunschwig and N. S. Lewis, *J. Phys. Chem. C*, 2012, **116**, 23569–23576.
- 24 C. J. Myall and D. Pletcher, *J. Chem. Soc., Perkin Trans. 1*, 1975, 953–955.
- 25 M. F. Hawthorne and R. N. Pilling, *Inorg. Synth.*, 1967, **9**, 16–19.
- 26 W. H. Knoth, H. C. Miller, J. C. Sauer, J. H. Balthis, Y. T. Chia and E. L. Muetterties, *Inorg. Chem.*, 1964, **3**, 159–167.
- 27 C. G. Zoski, *Handbook of electrochemistry*, Elsevier, Amsterdam, Boston, 2007.
- 28 K. Izutsu, *Electrochemistry in nonaqueous solutions*, Wiley-VCH, Weinheim, Germany, 2002.
- 29 N. G. Connelly and W. E. Geiger, *Chem. Rev.*, 1996, **96**, 877–910.
- 30 J. A. Davies, C. T. Eagle, D. E. Otis and U. Venkataraman, *Organometallics*, 1989, **8**, 1080–1088.
- 31 W. Einholz, K. Vaas and C. Wieloch, *Z. Anorg. Allg. Chem.*, 2002, **628**, 258–268.
- 32 E. A. Meulenkaamp, *J. Electrochem. Soc.*, 1997, **144**, 1664–1671.
- 33 M. L. Hitchman, *J. Electroanal. Chem.*, 1977, **85**, 135–144.
- 34 P. Lemasson, A. M. Baticle and P. Vennereau, *Surf. Sci.*, 1976, **59**, 177–194.
- 35 N. Vlachopoulos, P. Liska, J. Augustynski and M. Grätzel, *J. Am. Chem. Soc.*, 1988, **110**, 1216–1220.
- 36 R. Memming, *J. Electrochem. Soc.*, 1969, **116**, 785–790.
- 37 E. A. Shaede and M. C. R. Symons, *Can. J. Chem.*, 1973, **51**, 2492–2496.
- 38 *CRC handbook of chemistry and physics*, ed. W. M. Haynes, CRC Press, Boca Raton, FL, 91st edn, 2010.
- 39 I. V. Shimonis, *Elektrokhimiya*, 1973, **9**, 1787–1789.
- 40 D. V. Esposito, R. V. Forest, Y. C. Chang, N. Gaillard, B. E. McCandless, S. Y. Hou, K. H. Lee, R. W. Birkmire and J. G. G. Chen, *Energy Environ. Sci.*, 2012, **5**, 9091–9099.
- 41 H. S. White and A. J. Bard, *J. Am. Chem. Soc.*, 1982, **104**, 6891–6895.
- 42 J. F. Gibbons, G. W. Cogan, C. M. Gronet, N. S. Lewis, US Pat. no. 4764439A, 1988.
- 43 C. Xiang, A. C. Meng and N. S. Lewis, *Proc. Natl. Acad. Sci. U. S. A.*, 2012, **109**, 15622–15627.