

## A quantitative assessment of the competition between water and anion oxidation at WO<sub>3</sub> photoanodes in acidic aqueous electrolytes

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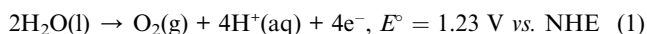
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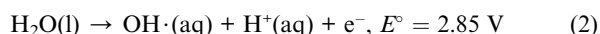
The faradaic efficiency for O<sub>2</sub>(g) evolution at thin-film WO<sub>3</sub> photoanodes has been evaluated in a series of acidic aqueous electrolytes. In 1.0 M H<sub>2</sub>SO<sub>4</sub>, persulfate was the predominant photoelectrochemical oxidation product, and no O<sub>2</sub> was detected unless catalytic quantities of Ag<sup>+</sup>(aq) were added to the electrolyte. In contact with 1.0 M HClO<sub>4</sub>, dissolved O<sub>2</sub> was observed with nearly unity faradaic efficiency, but addition of a hole scavenger, 4-cyanopyridine *N*-oxide, completely suppressed O<sub>2</sub> formation. In 1.0 M HCl, Cl<sub>2</sub>(g) was the primary oxidation product. These results indicate that at WO<sub>3</sub> photoanodes, water oxidation is dominated by oxidation of the acid anions in 1.0 M HCl, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub>, respectively.

### 1. Introduction

TiO<sub>2</sub> has received intense scrutiny<sup>1–7</sup> as a photoanode material in contact with aqueous electrolytes, both for water oxidation (eqn (1)) and for toxic waste remediation:



Due to the very positive potentials of the top of the valence band (VB) of metal oxide photoanodes, a prevailing mechanistic hypothesis is that the photoanodic reactions of such electrodes proceed through either free or surface-bound hydroxyl intermediates:<sup>1</sup>



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In strongly alkaline media, in which hydroxide has a high concentration and is the dominant anionic species, hydroxide is presumably readily oxidized by photogenerated holes to produce either free or surface-bound hydroxyl species, leading to the formation of H<sub>2</sub>O<sub>2</sub> and eventually to the production of O<sub>2</sub>(g) with near unity overall faradaic efficiencies ( $\eta$ ). Similar behavior has been observed in alkaline media for metal oxides such as Fe<sub>2</sub>O<sub>3</sub>,<sup>8–11</sup> which have smaller band gaps than TiO<sub>2</sub> and thus absorb more of the visible region of the solar spectrum. The photoelectrochemical behavior of such systems is consistent with the hypothesis that the valence band of these metal oxides is predominantly O 2p in character, resulting in a similar potential of the valence band edge for all of these metal oxides.<sup>12–14</sup>

In contrast, relatively few studies have elucidated the product distribution of metal oxide photoanodes when operated in acidic or neutral aqueous electrolytes. The reported faradaic efficiencies for O<sub>2</sub>(g) evolution,  $\eta(\text{O}_2)$ , at TiO<sub>2</sub>/electrolyte interfaces range from 0.09–0.35 in 0.2 M H<sub>2</sub>SO<sub>4</sub> under Xe arc lamp illumination<sup>7</sup> to 0.63–0.92 in 0.1–2.0 M NaOH using the 351- and 364-nm emissions of an Ar ion laser.<sup>6</sup> In some cases, low values for  $\eta(\text{O}_2)$  have been ascribed to the formation and accumulation of H<sub>2</sub>O<sub>2</sub>

### Broader context

Although many chemical fuels can be produced renewably from sunlight, O<sub>2</sub>(g) remains the only scalable oxidation product to balance the fuel-forming reactions, and thus the only scalable oxidant to release the chemical energy stored in these fuels. Semiconducting metal oxides (*e.g.*, TiO<sub>2</sub>) are known photoanode materials that evolve O<sub>2</sub>(g) in contact with aqueous electrolytes under solar illumination. The photoanodic reaction occurs in the absence of an oxygen evolution catalyst, and is generally presumed to involve hydroxyl radicals that are generated by energetic, photoinduced holes in the metal oxide. Herein we demonstrate that acid anions, such as Cl<sup>−</sup>(aq), HSO<sub>4</sub><sup>−</sup>(aq), and ClO<sub>4</sub><sup>−</sup>(aq), that are often considered inert, can be oxidized at WO<sub>3</sub>/electrolyte contacts, and effectively compete with water oxidation for the photoinduced holes. The chemical yields of O<sub>2</sub>(g) depend not only on the photocurrent, but also on the nature of the electrolyte and on the presence of additives in the electrolyte.

as an intermediate in the four-hole oxidation of two molecules of water to produce one molecule of  $O_2$ .<sup>7,15</sup>

$WO_3$  is an n-type metal oxide semiconductor<sup>16–24</sup> with an indirect band gap of 2.6–2.7 eV,<sup>25</sup> *i.e.*, responsive to the blue end of the visible spectrum ( $\lambda \leq 470$  nm). The electron Hall mobility in  $WO_3$  is  $\sim 12$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> at room temperature,<sup>26</sup> compared with  $\sim 0.3$  cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> for rutile  $TiO_2$ .<sup>27</sup> Extrinsic n-doping is therefore not required for  $WO_3$  to exhibit significant conductivity. Assuming an internal quantum yield of unity for all photons above the 2.6-eV band gap, the theoretically expected photocurrent density ( $J_{ph}$ ) for  $WO_3$  under 100 mW cm<sup>-2</sup> of global air mass (AM) 1.5 illumination is 5.0 mA cm<sup>-2</sup>. Unlike most semiconducting metal oxides (*e.g.*,  $TiO_2$ ,  $Fe_2O_3$ ,  $ZnO$ ),  $WO_3$  is acidic, and thus is resistant to photocorrosion at pH  $\leq 4$ ,<sup>15</sup> but dissolves in strongly alkaline solutions.

A widely accepted mechanism by which  $WO_3$  (and most other metal oxide photoanodes) produces photocurrent in aqueous electrolytes is that the powerfully oxidizing photogenerated holes, having a potential at the top of the valence band of  $\sim 3.0$  V *vs.* the normal hydrogen electrode (NHE), generate hydroxyl radicals (eqn (2)).<sup>20,28</sup> According to a computational study,<sup>29</sup> the hydroxyl radical is stabilized on  $WO_3$  surfaces, and the catalytic cycle for  $O_2(g)$  evolution is thermodynamically viable at a potential of  $\sim 2.3$  V *vs.* NHE. Most experimental studies have assumed that either eqn (1) or (2) is responsible for current flow at  $WO_3$  photoanodes in neutral and acidic solutions, as long as the electrolyte is thermodynamically more stable than water at the same pH value. In this work, we have conducted voltammetry, colorimetric assays, and fluorescence-based  $O_2$  detection to quantitatively evaluate the degree of competition between water oxidation (eqn (1) and (2)) and oxidation of other substrates, such as the acid anions of 1.0 M HCl,  $H_2SO_4$ , and  $HClO_4$ , when  $WO_3$  photoanodes are used under acidic conditions. The data indicate that the oxidation of  $Cl^-(aq)$ ,  $HSO_4^-(aq)$ , or  $ClO_4^-(aq)$  in the respective 1.0 M acid dominates the oxidation of water under such conditions, and no  $O_2(g)$  is produced directly at  $WO_3$  photoanodes.

## 2. Experimental

### Chemicals

Tungsten powder (Aldrich 510106,  $\geq 99.9\%$ ), 1.0 M hydrochloric acid (J. T. Baker 5620), and 4-cyanopyridine *N*-oxide (TCI America C0765,  $>98\%$ ) were used as received. Concentrated sulfuric acid (J. T. Baker 9681, 98%) and perchloric acid (Fisher A2286, 60%) were diluted to 1.0 M using deionized water (18 M $\Omega$ -cm resistivity) obtained from a Barnstead Nanopure system. All other chemicals were ACS reagents or higher purity.

### Electrochemistry

To form working electrodes, samples of  $SnO_2:F$ -coated glass slides (FTO, Hartford Glass, TEC 15) were cut into pieces 1.0 cm in width, and were cleaned with water and ethanol.  $WO_3$  or  $RuO_2$  was then deposited onto the slides. A Ag/AgCl/3.0 M NaCl electrode (Bioanalytical Systems, Inc.) was used as a reference and a Pt mesh was used as the counter electrode. To minimize contamination by NaCl, the reference electrode was isolated from the electrolyte by either a fine glass frit or by

a Luggin capillary. All potentials reported herein are relative to the normal hydrogen electrode (NHE), with the Ag/AgCl reference electrode taken to have a potential of  $E = 0.209$  V *vs.* NHE. Electrical contact to the working electrode was made either temporarily through a Cu clamp or permanently with Ga–In eutectic. An epoxy adhesive (Loctite Hysol 9460) was utilized for sealing metal leads on the glass slides, but was not used in contact with  $WO_3$  or  $RuO_2$ , to avoid oxidation of the epoxy. Voltammetric data were collected at a scan rate of 50 mV s<sup>-1</sup> with a BAS 100B electrochemical analyzer.

### $WO_3$ photoanodes

A clear, pale yellow solution of peroxytungstic acid (50 mM in W) in 30% (v/v) isopropanol/water<sup>30</sup> was stirred at room temperature for 24–48 h in the presence of a Pt mesh. The Pt mesh and isopropanol reduced the concentration of free  $H_2O_2$  to  $\sim 30$  ppm (as assessed using EM Quant peroxide test strips), which was required to produce  $WO_3$  films that displayed high photocurrent densities and fill factors. A conductive glass slide was then immersed in the peroxytungstic acid solution to a depth of 1.0 cm, and cathodic electrodeposition was performed, without stirring, at  $-0.50$  V *vs.* Ag/AgCl, using a BAS 100B electrochemical analyzer. Passage of a charge density of  $-0.25$  C cm<sup>-2</sup> (at a current density of  $-0.3$  mA cm<sup>-2</sup>) yielded a blue layer of  $WO_3 \cdot xH_2O$  on the electrode surface. The sample was then removed from the solution, rinsed with water and ethanol, and dried at 275 °C in air until the blue color had faded completely, typically requiring 5–10 min of drying time. The deposition–dehydration cycle was then repeated. After 3–6 cycles, the electrode was annealed at 500 °C in air for 1 h, yielding a pale yellow film of  $WO_3$  that displayed optical interference patterns to the naked eye. Profilometry (Dektak 3030) indicated that a three-layer  $WO_3$  film had a thickness of  $\sim 0.3$   $\mu$ m.

### Photoelectrochemistry

Measurements of the photoelectrochemical current density ( $J$ ) and photoelectrochemical electrolysis data were performed using simulated sunlight obtained from a 150 W Xe arc lamp, a beam collimator, and a global AM 1.5 filter (Oriel). The light intensity at the sample position was adjusted to produce the same photocurrent on a calibrated Si photodiode (Solarex) that would be produced by 100 mW cm<sup>-2</sup> of global AM 1.5 illumination. The electrolyte, the electrodes, and a magnetic stir bar were positioned in a 25 mL, three-neck round bottom flask that had been fitted with a fused silica window (25 mm in diameter) using an epoxy adhesive (Loctite Hysol 9460). The  $WO_3$  film faced the light source, but the Ag/AgCl reference electrode was not directly exposed to the simulated sunlight. The onset potential of the photoresponse ( $E_{on}$ ) was estimated at a scan rate of 10 mV s<sup>-1</sup> using a mechanical shutter (Electro-Optical Products Corp., SH-20) that chopped the simulated sunlight at 0.5 Hz. Bubbling of  $O_2(g)$  at 1.0 atm into the electrolyte had no effect on the  $J$ – $E$  characteristics of the  $WO_3$  photoelectrodes.

### Measurements of dissolved $O_2$

The  $O_2$  concentration in the anolyte was monitored using a fluorescence-based oxygen sensor (NeoFox, Ocean Optics). An

O<sub>2</sub>-sensitive fluorescent patch (HIOXY, Ocean Optics) on the sealed end of a glass tube was separated from the optical fiber inside the glass tube. The oxygen sensor was calibrated against a solution of air-saturated 1.0 M H<sub>2</sub>SO<sub>4</sub>, which was assumed to have an O<sub>2</sub> solubility of 7.7 mg L<sup>-1</sup> under 0.21 atm of O<sub>2</sub>(g) partial pressure.<sup>31</sup> The Pt counter electrode and the catholyte were housed in another glass tube that was isolated from the anolyte by use of a medium glass frit.

A RuO<sub>2</sub>-coated working electrode was prepared by drop-casting a 0.5% (w/v) solution of RuCl<sub>3</sub>·xH<sub>2</sub>O in isopropanol onto a conductive glass slide, and calcining at 400 °C in air for 1 h.<sup>32</sup> The working and counter electrodes, as well as the O<sub>2</sub> probe, were then hermetically mounted onto the reaction flask using polytetrafluoroethylene (PTFE) thermometer adapters that had O-ring seals (Ace Glass). The neck that housed the fluorescent probe was wrapped in black tape to block stray light from reaching the sensor. The flask was then filled entirely with Ar-saturated electrolyte (35 ml) and was cooled in a water bath at 20 ± 1 °C. Two-electrode (photo)electrolysis was then performed using a galvanostat (EG&G/PAR 362) interfaced to a computer. The baseline drift in the O<sub>2</sub> concentration was estimated immediately before and after the (photo)electrolysis and was compensated for in each experiment by linear extrapolation.

### Measurements of persulfate

Quantitative colorimetry was performed on a UV–visible spectrophotometer (Agilent 8453, 1-cm cuvette). To assay for ozone, a stream of Ar was passed through the anolyte and then into KI (2.00 mL, 2.0 mM in water). The free H<sub>2</sub>O<sub>2</sub> concentration was monitored at 410 nm in a mixture of the anolyte (1.00 mL) and titanium(IV) isopropoxide (20 µL of 50 mM solution in isopropanol). Peroxymonosulfate (HSO<sub>5</sub><sup>-</sup>) was measured by addition of KI (20 µL, 0.20 M in water) to the anolyte (2.00 mL), followed by measurement of the absorption at 350 or 370 nm within 30 s of mixing. The total peroxy concentration ([S<sub>2</sub>O<sub>8</sub><sup>2-</sup>] + [HSO<sub>5</sub><sup>-</sup>] + [H<sub>2</sub>O<sub>2</sub>]) was detected at 470 nm by mixing [Fe(SCN)<sub>6</sub>]<sup>4-</sup> (2.00 mL of 5.0 mM solution in 1.0 M H<sub>2</sub>SO<sub>4</sub>) and the anolyte (1.00 mL), and stabilizing the reading for 5–10 min. Working curves were established using known concentrations of Ce(SO<sub>4</sub>)<sub>2</sub>(aq) or H<sub>2</sub>O<sub>2</sub>.

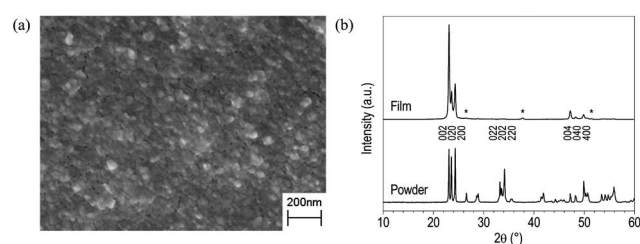
### Microscopy and X-ray diffraction (XRD)

Field emission scanning electron microscopy was performed on a Zeiss model 1550VP, and XRD data were collected with a PANalytical X'Pert using Cu-Kα excitation.

## 3. Results

### Thin-film WO<sub>3</sub> photoanodes

Fig. 1 shows a micrograph and an XRD pattern of a typical thin-film WO<sub>3</sub> photoanode. Annealing at 500 °C converted amorphous WO<sub>3</sub>·xH<sub>2</sub>O into WO<sub>3</sub> crystallites ~50 nm in size. As shown in Fig. 1b, bulk monoclinic WO<sub>3</sub> in the P2<sub>1</sub>/n space group<sup>33</sup> exhibits a powder XRD pattern that has systematically absent or attenuated (*hkl*) peaks, where at least one of *h*, *k*, and *l* is an odd number. However, the electrodeposited WO<sub>3</sub> thin films exhibited a further simplified XRD pattern, where only the (00*l*),



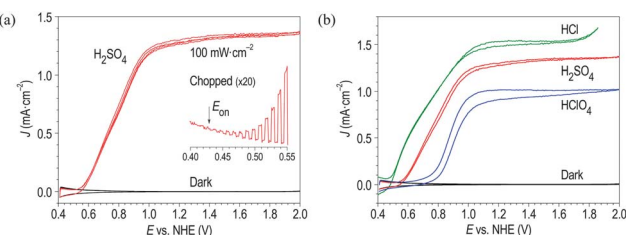
**Fig. 1** (a) Scanning electron micrograph and (b, top) X-ray diffraction pattern of a typical WO<sub>3</sub> thin film electrodeposited on conductive glass. Diffraction peaks due to the SnO<sub>2</sub>:F (FTO) coating are labeled by asterisks. (b, bottom) XRD of powdered WO<sub>3</sub> with indices is included for comparison.

(0*kl*0), and (*h*00) peaks (*h*, *k*, and *l* are even numbers) were observed, indicating that the (002), (020), or (200) crystallographic plane of the WO<sub>3</sub> crystallites was oriented nearly parallel to the glass substrate over a macroscopic area. The WO<sub>3</sub> crystallites were preferentially exposed through the (002) face, as evidenced by the fact that the (002) peak displayed the highest intensity.<sup>34</sup>

The WO<sub>3</sub> films produced by cathodic electrodeposition from peroxytungstic acid solutions were transparent, smooth, and adhered well to the conductive glass substrate. The as-deposited WO<sub>3</sub>·xH<sub>2</sub>O was an amorphous gel that was dark blue in color and was electrically conductive, both presumably due to the presence of free electrons in the film. The conductivity allowed for a relatively constant film growth rate. Upon dehydration, the volume of the WO<sub>3</sub>·xH<sub>2</sub>O film decreased significantly, producing cracks and peeling of the film.<sup>30</sup> This behavior was mitigated by repeated deposition and dehydration, because the small cracks that formed during a previous step of dehydration mended in a subsequent deposition step.

### Cyclic voltammetry in acids

Fig. 2 depicts the cyclic voltammetric behavior observed for WO<sub>3</sub> photoanodes in contact with a series of strong aqueous acids. As shown in Fig. 2a, in 1.0 M H<sub>2</sub>SO<sub>4</sub> under room light, referred to as “dark”, the WO<sub>3</sub> films produced small, capacitive current densities (<40 µA cm<sup>-2</sup>) for potentials up to 2.0 V vs. NHE. The photocurrent became significant (≥1 µA cm<sup>-2</sup>) at *E*<sub>on</sub> = 0.43 V



**Fig. 2** Cyclic voltammograms of WO<sub>3</sub> photoanodes in contact with 1.0 M aqueous strong acids. Conditions: (a) In 1.0 M H<sub>2</sub>SO<sub>4</sub>, under continuous or chopped simulated sunlight (global AM 1.5 illumination, 100 mW cm<sup>-2</sup>). The onset potential of photocurrent (*E*<sub>on</sub>) is indicated by an arrow. (b) WO<sub>3</sub> in 1.0 M HCl (green), H<sub>2</sub>SO<sub>4</sub> (red), and HClO<sub>4</sub> (blue), under simulated sunlight. Both panels also depict the results from control experiments in 1.0 M H<sub>2</sub>SO<sub>4</sub> in the dark (black).

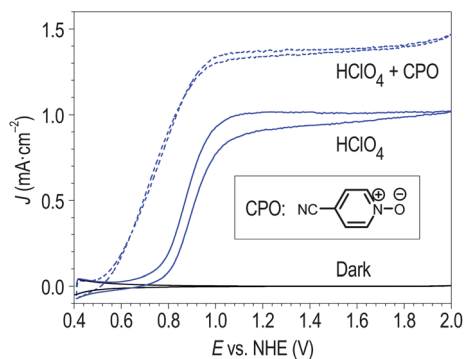
vs. NHE and reached a plateau value ( $J_{\text{ph}}$ ) at 1.0 V vs. NHE. Values of  $J_{\text{ph}} > 6 \text{ mA cm}^{-2}$  were recorded when the incident light intensity was increased beyond  $100 \text{ mW cm}^{-2}$ .

Fig. 2b compares the  $J$ - $E$  behavior observed for  $\text{WO}_3$  in contact with 1.0 M HCl,  $\text{H}_2\text{SO}_4$ , and  $\text{HClO}_4$ , respectively. After  $J$ - $E$  measurements under illumination in 1.0 M HCl, the  $\text{WO}_3$  photoanode exhibited a strong odor, and the Cu clamp in the headspace developed a blue-colored rust, both of which indicated the production of  $\text{Cl}_2(\text{g})$ . In contact with 1.0 M  $\text{HClO}_4$ , the  $\text{WO}_3$  photocurrent was not as stable as in contact with 1.0 M HCl or 1.0 M  $\text{H}_2\text{SO}_4$ , and a moderate decrease was detected between the forward and backward segments of a single scanning cycle. However, the performance of the electrode in 1.0 M  $\text{HClO}_4$  recovered fully after rinsing with water and drying in air, and the optical interference pattern of the  $\text{WO}_3$  thin film remained unchanged.

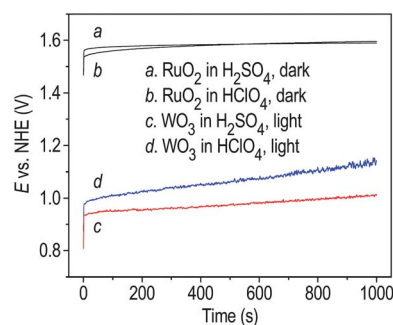
Fig. 3 depicts the effect of addition of 0.20 M 4-cyanopyridine *N*-oxide (CPO) on the  $J$ - $E$  behavior of the  $\text{WO}_3/1.0 \text{ M HClO}_4$  contact. CPO is a) not basic in character, having a conjugate  $\text{p}K_{\text{a}} = -0.73$ ;<sup>35</sup> b) chemically stable under such conditions in the dark, showing an irreversible oxidation at 2.51 V vs. NHE in  $\text{CH}_3\text{CN}$ ;<sup>36</sup> and c) transparent to visible light. Relative to the  $J$ - $E$  behavior depicted in 1.0 M  $\text{HClO}_4$  in Fig. 2b, addition of CPO produced stable photoelectrochemical behavior at the  $\text{WO}_3/1.0 \text{ M HClO}_4$  interface, and yielded a negative shift of 0.20 V in  $E_{\text{on}}$ , as well as a 35% increase in  $J_{\text{ph}}$  at  $100 \text{ mW cm}^{-2}$  of simulated global AM 1.5 illumination.

### Yields of dissolved $\text{O}_2$

A fluorescent-type probe was used to determine  $\eta(\text{O}_2)$  for  $\text{WO}_3$  electrodes under a series of acidic conditions during galvanostatic (photo)electrolysis for 1000 s at a current of 1.00 mA and a current density of  $1 \text{ mA cm}^{-2}$ . A  $\text{RuO}_2$  electrode (in the dark), also at a constant anodic current of 1.00 mA and a current density of  $1 \text{ mA cm}^{-2}$ , served as a control electrode for the production of  $\text{O}_2$ .<sup>32</sup> In separate three-electrode galvanostatic (photo)electrolysis experiments, which employed a  $\text{Ag}/\text{AgCl}$  reference electrode but not the  $\text{O}_2$  probe, the working electrode potential was 0.9–1.2 V vs. NHE for illuminated  $\text{WO}_3$  photoanodes, and was 1.5–1.6 V vs. NHE for  $\text{RuO}_2$  in the dark (Fig. 4).



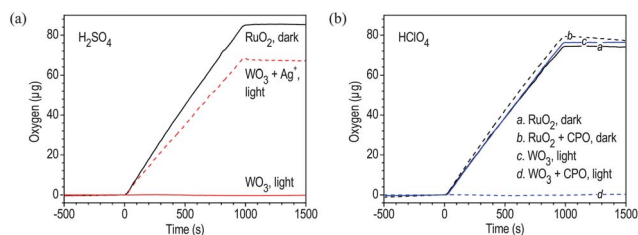
**Fig. 3** Cyclic voltammograms (dashed) of  $\text{WO}_3$  photoanodes in 1.0 M  $\text{HClO}_4$  with 0.20 M 4-cyanopyridine *N*-oxide (CPO, inset), under  $100 \text{ mW cm}^{-2}$  global AM 1.5 illumination. Control experiments in the absence of CPO or in the dark are also shown (solid lines).



**Fig. 4** The electrode potentials of a dark  $\text{RuO}_2$  electrode and of illuminated  $\text{WO}_3$  photoanodes during galvanostatic (photo)electrolysis (1.00 mA, 1000 s). Two electrolytes, 1.0 M  $\text{H}_2\text{SO}_4$  and 1.0 M  $\text{HClO}_4$ , were tested for each type of working electrode.

Fig. 5 shows that the  $\text{RuO}_2$  electrode displayed an  $\text{O}_2$  yield in close accord with the theoretically expected  $83 \mu\text{g}$  of  $\text{O}_2$  produced after passage of 1.00 C of anodic faradaic charge. The heterogeneous nature of the electrocatalysis was confirmed by the observation of  $\text{O}_2$  bubbles clinging to the  $\text{RuO}_2$  surface, even while stirring and under conditions at which the measured concentration of dissolved  $\text{O}_2$  was much lower than its solubility. The slightly lower  $\eta(\text{O}_2)$  in 1.0 M  $\text{HClO}_4$  relative to that observed in 1.0 M  $\text{H}_2\text{SO}_4$  could result from a systematic error, because the  $\text{O}_2$  sensor was calibrated against 1.0 M  $\text{H}_2\text{SO}_4$ .

The observed electrolysis products depended on the electrolyte and on the presence of additives in the solution. In pure 1.0 M  $\text{H}_2\text{SO}_4$ , no bubbles were observed on the  $\text{WO}_3$  photoanode, and the change in the  $\text{O}_2$  concentration was below the detection limit (0.02 ppm) of the fluorescent probe. When 0.050 mM  $\text{Ag}_2\text{SO}_4$  was added as a catalyst to the 1.0 M  $\text{H}_2\text{SO}_4$ , the  $\eta(\text{O}_2)$  increased to  $\sim 0.82$ . In a separate experiment, after photoelectrolyzing air-saturated 1.0 M  $\text{H}_2\text{SO}_4$  with 0.050 mM  $\text{Ag}_2\text{SO}_4$ , gas bubbles were visible on the walls of the flask and on the edges of the  $\text{WO}_3$  photoanode, but not on the  $\text{WO}_3$  surface. In contrast, in 1.0 M  $\text{HClO}_4$ ,  $\text{WO}_3$  under illumination produced  $\text{O}_2$  that was comparable with the amount produced by  $\text{RuO}_2$  in the dark. However, although bubbles were observed on the  $\text{RuO}_2$  electrode, no gas bubbles were observed on  $\text{WO}_3$  electrodes in 1.0 M  $\text{HClO}_4$ . The addition of 0.10 M CPO to 1.0 M  $\text{HClO}_4$  led to an undetectable  $\text{O}_2$  yield, and the anolyte turned pale brown after



**Fig. 5** Production of dissolved  $\text{O}_2$  during photoelectrolysis of (a) 1.0 M  $\text{H}_2\text{SO}_4$  and (b) 1.0 M  $\text{HClO}_4$  at constant currents (1.00 mA, 1000 s). A  $\text{RuO}_2$  electrode (black) yielded  $\text{O}_2$  at faradaic efficiencies near unity in the dark, whereas the products formed at illuminated  $\text{WO}_3$  photoanodes depended on the electrolyte (red or blue) and the additive (dashed): 0.050 mM  $\text{Ag}_2\text{SO}_4$  or 0.10 M 4-cyanopyridine *N*-oxide (CPO).

photoelectrolysis. The O<sub>2</sub> yield was not measured in 1.0 M HCl, because the fluorescent probe was not compatible with Cl<sub>2</sub>.

### Persulfate formation

Aliquots of the anolyte were withdrawn for colorimetric analyses after photoelectrolysis (1000 s at 1.00 mA) of air-saturated 1.0 M H<sub>2</sub>SO<sub>4</sub> (24 ml) using a WO<sub>3</sub> photoanode. The concentration of ozone was below the detection limit (1 ppm) of KI. The concentration of free H<sub>2</sub>O<sub>2</sub> was below the detection limit (0.1 ppm) of Ti (iv). The total persulfate (S<sub>2</sub>O<sub>8</sub><sup>2-</sup> + HSO<sub>5</sub><sup>-</sup>) concentration was determined, in two runs, to be 4.42 ± 0.05 μmol, corresponding to an η of 0.85 ± 0.01, which included a small contribution (0.05) from HSO<sub>5</sub><sup>-</sup>(aq). A control experiment indicated that ~10% of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) in 1.0 M H<sub>2</sub>SO<sub>4</sub> was hydrolyzed, producing HSO<sub>5</sub><sup>-</sup>(aq) after 1 day at room temperature.

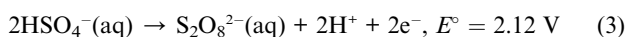
## 4. Discussion

### Competition between water and anion oxidation

The data and observations reported herein indicate that for WO<sub>3</sub> photoanodes operated in acidic aqueous electrolytes under simulated solar illumination, O<sub>2</sub> was either not formed at all or was a secondary oxidation product. When high values of η(O<sub>2</sub>) were observed, the O<sub>2</sub> bubbles were not localized on the electrode surface, in contrast to the case for the electrocatalytic oxidation of water to O<sub>2</sub>(g) effected by RuO<sub>2</sub> electrode surfaces. The interference pattern of WO<sub>3</sub> thin films remained identical to the naked eye after multiple experiments, which suggests that substantial photocorrosion of WO<sub>3</sub> photoanodes did not occur in 1.0 M H<sub>2</sub>SO<sub>4</sub>.

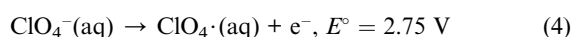
The absence of direct O<sub>2</sub> production indicates that other reductants effectively kinetically competed with water oxidation (eqn (1) and (2) for capture of photogenerated holes at WO<sub>3</sub> photoanodes under acidic conditions. The oxidation of Cl<sup>-</sup> to Cl<sub>2</sub> (E° = 1.36 V) in acidic and neutral water is a key step in the chloralkali process. The same reaction has been shown<sup>15</sup> to be driven by light at WO<sub>3</sub> photoanodes in contact with 1.0 M HCl. This hypothesis is consistent with the indications of Cl<sub>2</sub>(g) production for WO<sub>3</sub>/1.0 M HCl contacts.

In H<sub>2</sub>SO<sub>4</sub> solutions, an analogous anion-derived hole-transfer process occurs at a Pt anode in the dark,



with η(S<sub>2</sub>O<sub>8</sub><sup>2-</sup>) up to 0.90.<sup>37</sup> The observations described herein indicate that eqn (3) dominated the oxidative processes at WO<sub>3</sub> photoanodes in 1.0 M H<sub>2</sub>SO<sub>4</sub>, where S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) and its hydrolysis product HSO<sub>5</sub><sup>-</sup>(aq), instead of O<sub>2</sub>(g), were the only detectable photoelectrochemical products. A prior study<sup>15</sup> reported that considerable amounts of O<sub>2</sub>(g) were collected after 4 h of unfiltered Hg lamp irradiation of WO<sub>3</sub> anodes in 0.5 M H<sub>2</sub>SO<sub>4</sub>, but this observation can be attributed to photo-degradation of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq), because S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) strongly absorbs at 254 nm.<sup>38</sup>

In 1.0 M HClO<sub>4</sub>, the perchlorate radical could initially be formed,



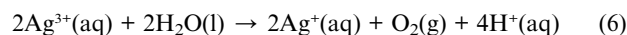
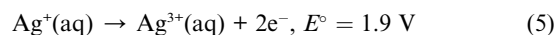
as has been identified in nonaqueous electrochemistry.<sup>39,40</sup> In aqueous solutions, the ClO<sub>4</sub><sup>·</sup> radical does not form stable peroxy species, and yields O<sub>2</sub> as a final oxidation product. The temporary decrease in photocurrents during the operation of WO<sub>3</sub> in 1.0 M HClO<sub>4</sub> could be due to weak binding of ClO<sub>4</sub><sup>·</sup> to active sites on the WO<sub>3</sub> surface. This behavior thus agrees with the observations that high values of η(O<sub>2</sub>) were obtained during the operation of WO<sub>3</sub> as a photoanode in 1.0 M HClO<sub>4</sub>, but the O<sub>2</sub> was produced homogeneously in the solution and not primarily at the solid/liquid interface.

The distinct cyclic voltammograms (Fig. 2b) observed in 1.0 M HCl, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub>, respectively, provide additional evidence that the current-limiting process at the WO<sub>3</sub> photoanode involved reactions with the anions of these electrolytes (Fig. 6) as opposed to direct oxidation of water. The value of E<sub>on</sub> is affected by the semiconductor properties of WO<sub>3</sub> as well as by the redox potential of the electrolyte,<sup>41</sup> so the variation of E<sub>on</sub> in these acids cannot be simply estimated from the E° values for oxidation of the acid anion. E<sub>on</sub> also depends on the solution pH, due to protonation of the WO<sub>3</sub> surface.<sup>42</sup>

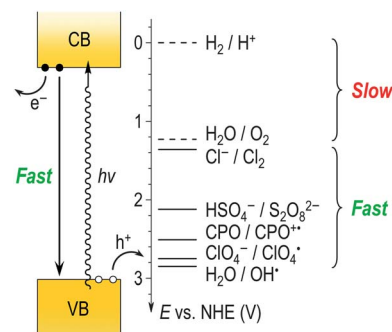
Although H<sub>3</sub>PO<sub>4</sub> solutions were not evaluated in our work, in view of the low acidity of phosphoric acid, the stable peroxy-diphosphate (P<sub>2</sub>O<sub>8</sub><sup>4-</sup>) species, instead of O<sub>2</sub>(g), would be expected to be formed at illuminated WO<sub>3</sub>/H<sub>3</sub>PO<sub>4</sub> interfaces.

### Effect of additives

The final product distribution can of course be modified by additives that can catalyze secondary reactions in the solution (Fig. 5). For example, Ag<sup>+</sup> is a facile two-electron redox catalyst that regenerates HSO<sub>4</sub><sup>-</sup>(aq) from S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq), with concomitant evolution of O<sub>2</sub>:<sup>43</sup>

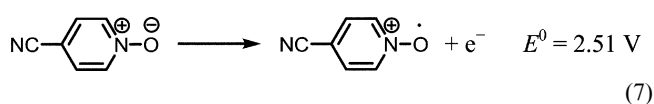


In 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions, SO<sub>4</sub><sup>2-</sup> coordinates Ag<sup>+</sup> and Ag<sup>3+</sup> at low concentrations, and no cathodic current due to the electroplating of Ag(s) on WO<sub>3</sub> occurred in the dark. The above reaction scheme is fully consistent with the detection of high η(O<sub>2</sub>) in 1.0 M H<sub>2</sub>SO<sub>4</sub> solutions that contained Ag<sup>+</sup>, while no O<sub>2</sub> was detected during the photoelectrolysis of pure 1.0 M H<sub>2</sub>SO<sub>4</sub>.



**Fig. 6** Redox couples accessible to photogenerated holes in the valence band (VB) of WO<sub>3</sub>. The reactions that involve the H<sub>2</sub>/H<sup>+</sup> and H<sub>2</sub>O/O<sub>2</sub> couples have very slow rates in the absence of a catalyst.

A useful probe molecule is 4-cyanopyridine *N*-oxide (CPO), which can act as a scavenger for energetic holes but is not a sacrificial reagent:



Because of its relatively positive oxidation potential, CPO did not interfere with O<sub>2</sub>(g) evolution at a RuO<sub>2</sub> electrode in 1.0 M HClO<sub>4</sub>, and O<sub>2</sub>(g) was evolved at 1.5–1.6 V vs. NHE (Fig. 4). However, on WO<sub>3</sub> photoanodes, oxidation of CPO effectively competed with the oxidation of water or ClO<sub>4</sub><sup>-</sup>, substantially enhancing the apparent *J*–*E* performance (Fig. 3). The chemical energy stored in CPO<sup>•+</sup>, however, results in decomposition of CPO<sup>•+</sup> rather than in the oxidation of water to O<sub>2</sub>(g).

### Photoanode efficiencies

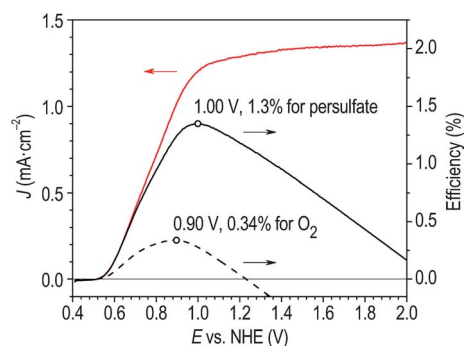
The energy-conversion efficiency of a photoanode oxidizing a reduced species, A<sup>-</sup>, to produce an oxidized species, A, that could in turn be reversibly converted back to A<sup>-</sup> by reduction at an ideally nonpolarizable electrode, in a regenerative cell configuration, is given by:

$$\text{Efficiency} = \frac{J[E(A/A^-) - E]}{P_{\text{in}}} \quad (8)$$

where *P*<sub>in</sub> is the illumination power density, *J* is the photocurrent density, *E* is the applied photoanode potential, and *E*(A/A<sup>-</sup>) is the redox potential of the species being oxidized. Instead, when a chemical product is made at the photoanode, *E*(A/A<sup>-</sup>) is the redox potential at which the chemical product would be produced at an ideally nonpolarizable, kinetically reversible anode in the dark.

Clearly, for a specific *J*–*E* behavior of the photoanode vs. a fixed reference electrode, the calculated energy-conversion efficiency of the photoelectrode will depend critically upon the value of *E*(A/A<sup>-</sup>). For example, if O<sub>2</sub>(g) is produced by a photoanode, the relevant value of *E*(O<sub>2</sub>/H<sub>2</sub>O) in eqn (8) under standard conditions is 1.23 V vs. NHE, whereas if a species with a more positive redox potential (*e.g.*, persulfate) is produced, the identical photoanodic *J*–*E* behavior would in fact correspond to a higher efficiency for the photoanode. This situation occurs because persulfate has a much more positive potential, *E*<sup>o</sup>(S<sub>2</sub>O<sub>8</sub><sup>2-</sup>/HSO<sub>4</sub><sup>-</sup>) = 2.12 V, and is much more oxidizing than O<sub>2</sub>, so more energy is stored chemically by production of persulfate than by production of O<sub>2</sub>. Of course, realization of the full energy content of the oxidized product would require either a reversible chemical reaction, or a fuel cell operating at the reversible potential for producing the reduced species A<sup>-</sup> from the oxidized species A that was produced by oxidation at the photoanode.

For WO<sub>3</sub> photoanodes in contact with 1.0 M HCl, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub>, the predominant oxidation products are Cl<sub>2</sub>(g), S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq), and O<sub>2</sub>(g), so *E*<sup>o</sup> = 1.36, 2.12, and 1.23 V, respectively. These values would therefore represent the relevant redox potentials to use in eqn (8) to calculate the efficiency for WO<sub>3</sub> photoanodes in each case under standard conditions. Fig. 7 plots the efficiency-potential characteristics of WO<sub>3</sub> in contact with 1.0 M H<sub>2</sub>SO<sub>4</sub>, calculated using two possible values of *E*<sup>o</sup>, 2.12 or



**Fig. 7** Current density–potential (red) and efficiency–potential (black) behavior of WO<sub>3</sub> photoanodes in 1.0 M H<sub>2</sub>SO<sub>4</sub>. The apparent efficiencies were evaluated assuming that S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) (solid) or O<sub>2</sub>(g) (dashed) was the photoanodic product. In each case, the maximum apparent efficiency is indicated at the corresponding potential.

1.23 V, in eqn (8). The assumption that O<sub>2</sub>(g) is the anodic product and that *E*<sup>o</sup> = 1.23 V at the WO<sub>3</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub> interface would lead to an underestimation of the efficiency, and would produce a maximum efficiency of 0.34% at *E* = 0.90 V. Instead, adopting *E*<sup>o</sup> = 2.12 V yields a maximum efficiency of 1.3% at *E* = 1.00 V. Note that this maximum value represents a lower limit of the internal efficiency of the WO<sub>3</sub>/1.0 M H<sub>2</sub>SO<sub>4</sub> contact, because the WO<sub>3</sub> thin films used in this study were not optically dense and thus did not absorb all of the incident photons above the 2.6-eV band gap.

### Implications for other metal oxide photoanodes

In an analogous fashion to the photoelectrochemical behavior of WO<sub>3</sub> photoanodes in 1.0 M H<sub>2</sub>SO<sub>4</sub> reported herein, an illuminated single-crystalline TiO<sub>2</sub> electrode in contact with several 2 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>–H<sub>2</sub>SO<sub>4</sub> electrolytes has been reported to produce S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) with  $\eta = 0.25$ – $0.32$ , but no H<sub>2</sub>O<sub>2</sub> was detected.<sup>44</sup> This behavior suggests that the initial oxidation product at TiO<sub>2</sub> in sulfate solutions, under acidic and near-neutral conditions, is also persulfate, as opposed to hydroxyl radical. The low  $\eta$ (O<sub>2</sub>) measured for TiO<sub>2</sub>/H<sub>2</sub>SO<sub>4</sub>(aq) contacts<sup>6</sup> is not attributable to the formation and accumulation of H<sub>2</sub>O<sub>2</sub>. By extension, other metal oxide (*e.g.*, titanates and tantalates) photoanodes operating in acidic solutions of HCl or H<sub>2</sub>SO<sub>4</sub> may well also predominantly produce Cl<sub>2</sub>(g) or S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq), respectively, as opposed to O<sub>2</sub>(g) or H<sub>2</sub>O<sub>2</sub>, as primary or secondary oxidation products.

## 5. Conclusions

The anodic reactions at illuminated WO<sub>3</sub> thin films in contact with 1.0 M HCl, H<sub>2</sub>SO<sub>4</sub>, and HClO<sub>4</sub> were quantitatively analyzed from three perspectives: the *J*–*E* characteristics were monitored by voltammetry, the yield of dissolved O<sub>2</sub> was monitored by fluorescence quenching, and the yields of S<sub>2</sub>O<sub>8</sub><sup>2-</sup>(aq) and H<sub>2</sub>O<sub>2</sub> were monitored using colorimetry. For all three of these acidic aqueous electrolytes, oxidation of the respective acid anion, rather than water oxidation, was the predominant process at WO<sub>3</sub> photoanodes. Homogeneous O<sub>2</sub>(g) evolution from the electrolyte solution, a secondary reaction that

was not directly probed by measurement of the photoelectrochemical behavior of the anode, occurred in pure 1.0 M HClO<sub>4</sub>, as well as in 1.0 M H<sub>2</sub>SO<sub>4</sub> that contained Ag<sup>+</sup>(aq) as a catalyst. In 1.0 M HClO<sub>4</sub>, a hole scavenger, CPO, blocked the oxidation of ClO<sub>4</sub><sup>-</sup>(aq) or water at WO<sub>3</sub> photoanodes, but had no effect on the electrocatalytic oxidation of water effected by RuO<sub>2</sub> in the dark. This rule of “anion priority” can be extended to the photoanodic oxidation of OH<sup>-</sup>(aq) in strongly alkaline solutions, and may well apply to other metal oxide photoanodes operating in acidic or near-neutral aqueous electrolytes.

## 6. Acknowledgements

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