Improving O₂ Production of WO₃ Photoanodes with IrO₂ in Acidic Aqueous Electrolyte

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Supporting Information

Electrode Illumination Schematic.



Figure S1. Schematic for OER catalyst/WO₃/FTO/glass photoanodes. Under front illumination conditions, the light was passed through the catalyst layer before getting to the photoactive WO₃. Under back illumination conditions, the light passed through the highly transparent glass substrate and FTO back contact before absorption in the WO₃ layer, without first passing through the catalyst.

IrO₂ on WO₃ Contact.



Figure S2. *J-E* behavior for WO₃ on W foil. Photoelectrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H_2SO_4 for (a) front-illuminated (black line) WO₃ on FTO, (red line) front-illuminated WO₃ on W foil, and (gray line) WO₃ on W foil in the dark. (b) Dark *J-E* behavior for (black line) sputtered IrO₂ on FTO, (green line) sputtered IrO₂ on WO₃/W foil, and (gray line) WO₃/W foil.

To ensure that the electrocatalytic current observed on WO₃ photodiodes in reverse bias at > 1.4 V vs. RHE was not due to a shunt caused by IrO₂ deposited directly in contact with the FTO substrate, WO₃ on W foil electrodes were fabricated. By annealing these electrodes in air at 400 °C for 2 hr, all exposed substrate at the bottom of the nanopores and cracks in the bulk WO₃ was oxidized to WO₃ as well. This was demonstrated by the lack of shunting in an electrolyte with a fast, one-electron redox couple (Fig. 1). During sputtering of IrO₂, a mask was used to deposit the catalyst only on the WO₃ film to avoid any contact with the W foil or any edge effects. Nevertheless, as demonstrated in Figure S2b, sputtered IrO₂/WO₃/W foil electrodes displayed electrocatalytic current similar to IrO₂ by itself. The shunt therefore was interpreted to occur through the WO₃ layer.



Figure S3. Solid-state cyclic voltammogram for IrO₂ contacts on WO₃. Current vs. voltage (*I-V*) behavior for two-electrode CV sweeps at 100 mV s⁻¹ using sputtered IrO₂ contact pads 1 mm apart on WO₃ on glass (without FTO), scanning from (black lines) -0.5 to 0.5 V and from (blue lines) -1.0 to 1.0 V.

To verify the finding of ohmic behavior between the IrO_2 catalyst and WO_3 semiconductor, an attempt was made to directly investigate the nature of the contact with a solid-state measurement. WO_3 was deposited on a cleaned glass slide without an underlying transparent conductive layer, then two IrO_2 contact pads were deposited on the WO_3 by sputtering for 30 min using a mask to define square spots spaced 1 mm apart. A coiled Cu wire was attached to each IrO_2 spot with Ag paint, and these wires were used in two-electrode cyclic voltammograms at various scan rates and potentials. As shown in Figure S3, the resulting currents were low (in the μ A range) due to the high resistance of the WO_3 layer. Hysteresis in the data was ascribed to capacitance in the WO_3 layer. Still, the overall trend across a 2 V range was quite linear, an indication of ohmic behavior.

Co₃O₄ and RuO₂ Catalyst Layers.

In addition to IrO_2 , the OECs Co_3O_4 and RuO_2 were tested as drop-casted, sintered films and as sputtered films. Due to their instability in the 1 M H_2SO_4 electrolyte used in this work, they were not explored further.

For the drop-cast, sintered catalyst electrodes, three different oxygen-evolving metal oxide catalysts (IrO₂, RuO₂, or Co₃O₄) were separately deposited onto thin WO₃ films by drop-casting solutions of metal salts and then sintering to achieve the oxide form. A micropipette was used to drop-cast 20 μ L of a 20 mM solution of the corresponding metal salt (IrCl₃'3H₂O from Fisher Scientific, RuCl₃'xH₂O from Alfa Aesar) in isopropanol on a ~1 cm² area of the WO₃. These films were allowed to dry at room temperature for ~ 1 hr then sintered at 400 °C in air for 1 hr. Analogous electrodes of the OEC directly on FTO glass were produced by the same method.

For the sputtered catalyst electrodes, OEC films of IrO₂, RuO₂, or Co₃O₄ were sputtered from metal targets of Ir, Ru, or Co (all \geq 99.9% from AJA International), respectively. In each case, the catalyst layer was sputtered onto the WO₃ film from an RF source at 200 W at 300 °C under a constant flow of 3.0/3.0 sccm Ar/O₂ for IrO₂ and 4.5/0.5 sccm Ar/O₂ for RuO₂ and Co₃O₄ while maintaining an overall pressure of 6 mtorr. Two different thicknesses of each catalyst were produced by sputtering for either 0.5 min (< 10 nm) or 30 min (> 100 nm). Analogous electrodes of the OEC directly on FTO glass were produced by the same method.



Figure S4. Instability of Co₃O₄ during cyclic voltammetry. *J*-*E* behavior in 1 M H₂SO₄ of (a) sintered Co₃O₄ on WO₃ over 6 scans, and (b) sputtered Co₃O₄ on FTO/glass over 4 scans. Thin, 0.5 min sputtered Co₃O₄ decayed rapidly over 4 scans (black to gray lines). Although thick, 30 min sputtered Co₃O₄ (red line) appeared stable over 4 scans, the current decayed away after extended use (> 1 hr) in 1 M H₂SO₄.



Figure S5. *J-E* behavior for drop-cast, sintered OER catalysts on WO₃. Photoelectrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H_2SO_4 for (a) Co_3O_4 , (b) RuO₂, and (c) IrO₂ sintered from drop-cast metal salt solutions on WO₃ thin films and annealed in air at 400 °C for 1 hr. Performance is shown for (green lines) back illumination, (red lines) front illumination, and (gray lines) in the dark, with (blue lines) bare WO₃ under illumination and (black lines) the catalyst by itself in the dark for reference.



Figure S6. XPS of sputtered OER catalyst films on WO₃ photoanodes. High resolution scans for sputtered (a,d) Co_3O_4 , (b,e) RuO_2 , and (c,f) IrO_2 on WO₃ thin films. The (a-c) O 1s, (d) Co 2p, (e) Ru 3d, and (f) Ir 4d regions are shown. The RuO_2 and IrO_2 films were sputtered for 0.5 min, but the Co_3O_4 film was sputtered for 30 min to obtain a better Co 2p signal for clearer peak fitting.



Figure S7. *J-E* behavior for sputtered OER catalyst on WO₃. Photoelectrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H_2SO_4 for (a,c) 0.5 min sputtered and (b,d) 30 min sputtered films of (a,b) Co_3O_4 , and (c,d) RuO_2 on WO₃. Performance is shown for (green lines) back illumination, (red lines) front illumination, and (gray lines) in the dark, with (blue lines) bare WO₃ under illumination and (black lines) the catalyst by itself in the dark for reference.



Figure S8. Dark *J-E* behavior for sputtered OER catalysts. Dark electrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H_2SO_4 for (black) FTO, (gray) WO₃, (light red, dashed) thin sputtered Co_3O_4 , (dark red) thick sputtered Co_3O_4 , (light green, dashed) thin sputtered RuO₂, (dark green) thick sputtered RuO₂, (light blue, dashed) thin sputtered IrO₂, and (dark blue) thick sputtered IrO₂.



Optical Transmittance for Sintered and Sputtered IrO₂ Layers.

Figure S9. Optical transmission of IrO_2 catalyst layers. The percent of light transmitted vs. wavelength for sintered and sputtered IrO_2 layers on (a) FTO/glass substrates and (b) baseline-corrected for FTO/glass substrates to determine transmission only through the IrO_2 layer.

Annealing Sputtered IrO₂/WO₃ Photoanodes.



Figure S10. *J-E* behavior for annealed, sputtered IrO_2 on WO_3 . Photoelectrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H₂SO₄. Performance is shown for 30 min sputtered IrO_2/WO_3 (red lines) as-deposited and (green lines) annealed under back illumination, with (blue lines) bare WO₃ under illumination and (black lines) the catalyst by itself in the dark for reference. Annealed samples were heated in air at 400 °C for 30 min.



Figure S11. Morphology of sputtered IrO_2 layer. Cross-sectional TEM images for 30 min sputtered IrO_2 on WO₃ with a scale bar of (a) 200 nm, (b) 30 nm, and (c) 5 nm.

O₂ Production Measurements.



Figure S12. O₂ **production of a bare WO**₃ **photoanode.** The amount of O₂ produced by a bare, sputtered WO₃ film in 1 M H₂SO₄ under illumination while biased at a given potential, as determined by (dashed lines) the total charge passed (assuming 100% faradaic conversion to O₂) and by (solid lines) an optical O₂ sensor. The WO₃ photoanode was biased at potentials of (green lines) 1.4 V, (red lines) 1.5 V, (blue lines) 1.6 V, and (black lines) 2.0 V vs. RHE.



Figure S13. O₂ production of sputtered OER catalysts on WO₃. The amount of O₂ produced at 1.2 V vs. RHE under back illumination in 1 M H₂SO₄ for a WO₃ photoanode with a sputtered catalyst film of (a) Co₃O₄, and (b) RuO₂. The quantity of O₂ was determined by (dashed lines) the total charge passed (assuming 100% faradaic conversion to O₂) and by (solid lines) an optical O₂ sensor. For catalyst thicknesses, (red lines) a thin film was sputtered for 0.5 min, and (blue lines) a thick film was sputtered for 30 min. To demonstrate the high faradaic efficiency achievable with each catalyst, (black lines) bare catalyst films were measured in the dark at 1.5 V vs. RHE (RuO₂) or 1.7 V vs. RHE (Co₃O₄).

Electrode Stability.



Figure S14. XPS of sputtered OER catalysts on WO₃. High resolution XPS spectra for WO₃ films covered with (a, c, e) Co_3O_4 , and (b, d, f) RuO_2 , each sputtered for 0.5 min. The regions shown are (a,b) W 4f, (c,d) O 1s, (e) Co 2p, and (f) Ru 3d. The films were analyzed (black lines) as-deposited, and (red lines) after a *J*-*E* behavior measurement under illumination in 1 M H₂SO₄.

Figure S14 shows the XPS spectra for thin, 0.5 min sputtered OEC/WO₃ electrodes in which the catalyst layer was thin enough to allow sampling of the underlying WO₃. As expected from the decay in current observed during *J*-*E* measurements (Fig. S4), the Co_3O_4 Co 2p signal is completely gone after measurement in 1 M H₂SO₄ (Fig. S14e). Although the catalytic current with RuO₂ was much steadier, the XPS results reveal that this OEC was not long-term stable in strong acid either. After measuring the *J*-*E* behavior, the W 4f peaks of the RuO₂/WO₃ sample became more intense (Fig. S14b) and the O 1s peak changed such that the WO₃ component became more prominent relative to the RuO_x component (Fig. S14d and Fig. S6b), indicating the gradual dissolution of the RuO₂ layer.



Figure S15. Stability of WO₃ photoanodes. (a) Current density vs. time measurement for bare WO₃ in 1 M H₂SO₄ under 1 sun AM1.5 illumination at 1.2 V vs. RHE with cyclic voltammetric (CV) measurements (30 mV s⁻¹ scan from 0.4 to 2.0 V vs. RHE and back, 2 scans) made every hour. The discontinuities in the curve are due to the CV measurements. (b, c) XPS data for sputtered WO₃ films (black lines) as-deposited and (red lines) after 12 hr at 1.2 V vs. RHE in 1 M H₂SO₄ under 1 sun AM1.5 illumination showing high resolution scans of (b) the W 4d region and (c) the O 1s region.



Figure S16. Stability of sputtered IrO_2 on WO₃. XPS spectra of the W 4f region of thin, 0.5 min sputtered IrO_2 on WO₃, showing (a) the sequential change from (black lines) as-deposited to (red lines) after a *J*-*E* behavior measurement under illumination in 1 M H₂SO₄, to (blue lines) after 12 hr at 1.2 V vs. RHE under illumination in 1 M H₂SO₄. Also shown are (b) the fitted peaks for the sample after 12 hr at 1.2 V vs. RHE under illumination in 1 M H₂SO₄.



Figure S17. XPS comparison of different IrO₂ deposition methods. XPS spectra of the O 1s region of WO₃ with IrO₂ deposited on it by (black line) drop-casting an IrCl₃ solution and then sintering at 400 °C for 1 hr, (red line) electrodeposition, (blue line) electrodeposition followed by a 400 °C anneal for 1 hr, and (green line) sputtering for 0.5 min.

Electrodeposited IrO₂ on WO₃ Photoanodes.



Figure S18. *J-E* behavior for electrodeposited IrO_2 on WO_3 by the method of Zhao et al.¹ Photoelectrochemical current-density (*J*) vs. potential (*E*) behavior in 1 M H₂SO₄ for electrodeposited IrO_2 on WO₃ (a) as-deposited and (b) after a 400 °C anneal for 1 hr. Performance is shown for (green lines) back illumination, (red lines) front illumination, and (gray lines) in the dark, with (blue lines) bare WO₃ under illumination and (black lines) the catalyst by itself on FTO in the dark for reference. Multiple successive scans of IrO_2/WO_3 in the dark and IrO_2 on FTO are included to demonstrate unstable current in (a) and stable current in (b).

For this IrO_2 electrodeposition procedure, colloidal IrO_x in a pH 1 mixture was prepared as published.¹ The solution was stored in a refrigerator at 4 °C. IrO_x films were deposited on FTO/glass and on WO₃ by maintaining the potential at 1.4 V vs. Ag/AgCl until 2.5 C of charge had been passed. In each case, the exposed area of the working electrode for deposition was 1 cm². During deposition, the solution was stirred vigorously and kept in an ice bath.

Drop-cast, Particulate IrO₂ on WO₃ Photoanodes. Another method tested for IrO₂ catalyst attachment was the drop-casting of IrO₂ powders directly on the WO₃ surface. IrO₂ powder (99%, Alfa Aesar) was mixed to a 30% w/w IrO₂ suspension in isopropanol and then sonicated for > 3 hr before drop-casting 20 μ L of the suspension onto a 1 cm² WO₃ electrode area using a micropipette and drying in ambient for ~ 1 hr. Eight sequential coatings of IrO₂ particles were applied. Some particulate IrO₂/WO₃ electrodes were also annealed at 500 °C for 2 hr in air. Analogous electrodes of IrO₂ particles directly on FTO glass were produced by the same method.

Before any annealing step, particulate IrO_2/WO_3 photoanodes performed comparably to bare WO_3 under back illumination, but with the photocurrent was reduced by 68% due to catalyst light absorption under front illumination (Table 1). However, these samples displayed no O_2 production and had issues with catalyst loss due to poor adhesion. After annealing to sinter the catalyst particles to the WO_3 surface, most IrO_2 particles remained attached during testing. A reduction in photocurrent was observed after the high temperature anneal, but the faradaic oxygen production efficiency increased from 0 to 43% (Table 1). Considering the relatively low O_2 yield compared to the percentage of photocurrent lost under front illumination, this catalyst attachment method was not pursued further. However, a more sophisticated technique to pattern IrO_2 particles at set dimensions to optimize catalytic activity relative to optical absorption may still hold promise for future studies.

^{1.} Y. X. Zhao, E. A. Hernandez-Pagan, N. M. Vargas-Barbosa, J. L. Dysart and T. E. Mallouk, J. Phys. Chem. Lett., 2011, 2, 402-406.