Electronic Supplementary Information for

Improving the Stability and Selectivity for the Oxygen-Evolution Reaction on Semiconducting WO_3 Photoelectrodes with a Solid-State FeOOH Catalyst

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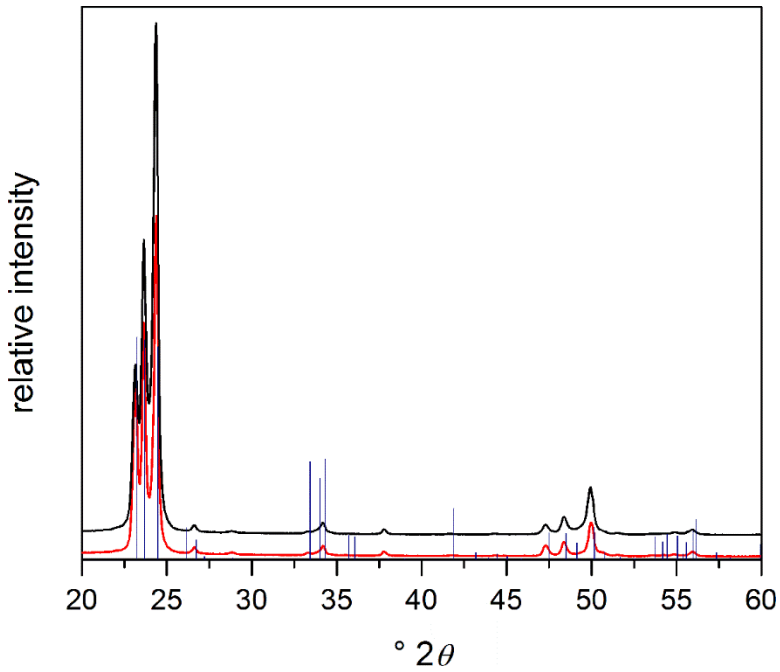

Fig. S1. Powder XRD pattern of WO_3 (black) and WO_3-FeOOH (red). Blue vertical lines represent indexed Bragg reflections for monoclinic WO_3.

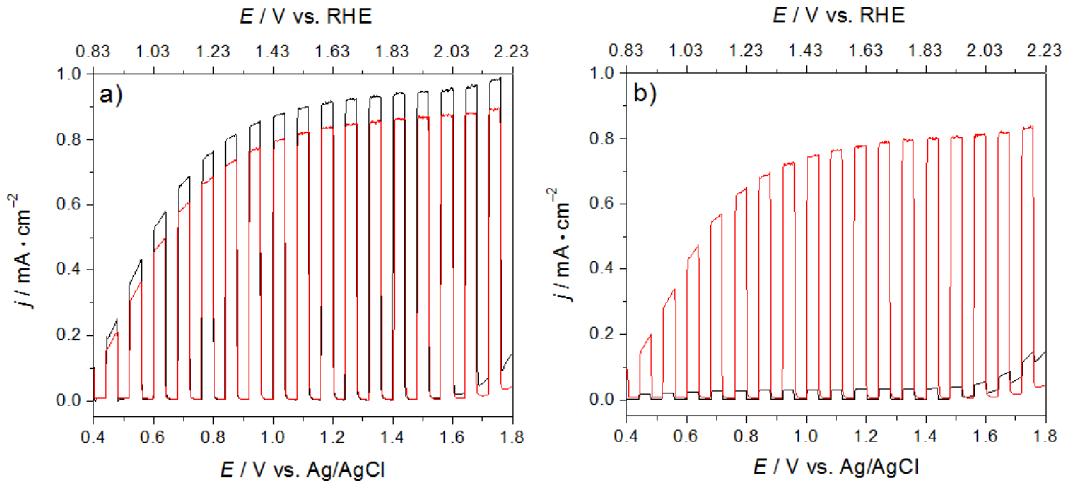

Fig. S2. CL-LSVs of WO_3 recorded before (red) and after (black) soaking 0.1 M KP_i buffer at a) pH 4; and b) pH 7.

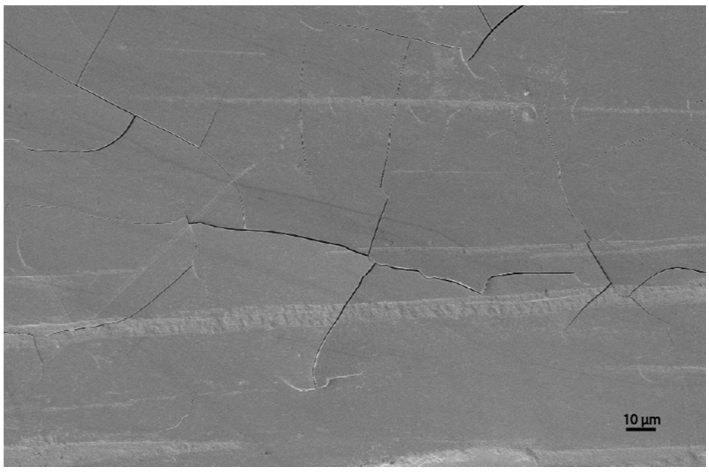

Fig. S3. SEM image of a cracked FeOOH on WO_3. The pictured film was synthesized using longer deposition times, generating a thicker layer. Cracking in the film was observed due to the film drying out.

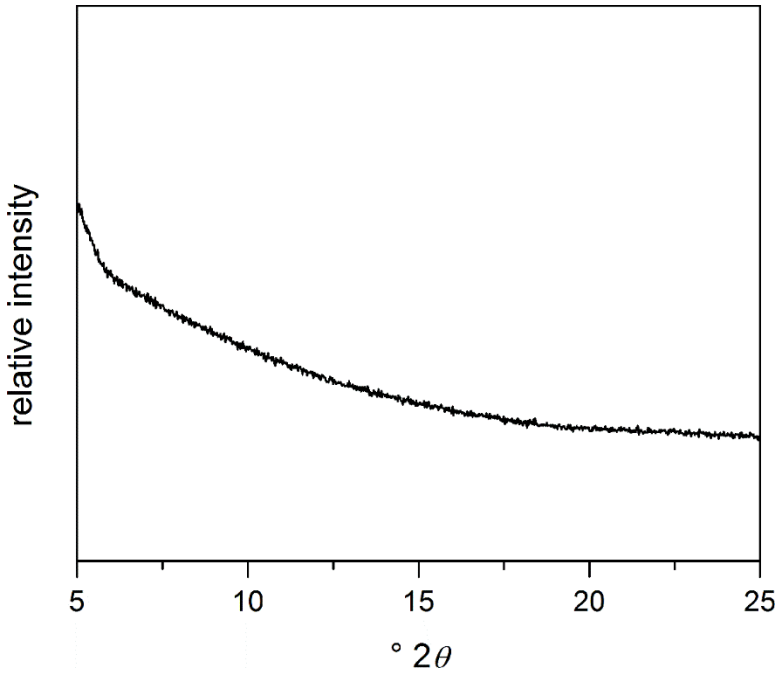

Fig. S4. Powder XRD pattern of FeOOH electrochemically deposited onto FTO showing no discernible Bragg reflections due to the amorphous nature of the film.

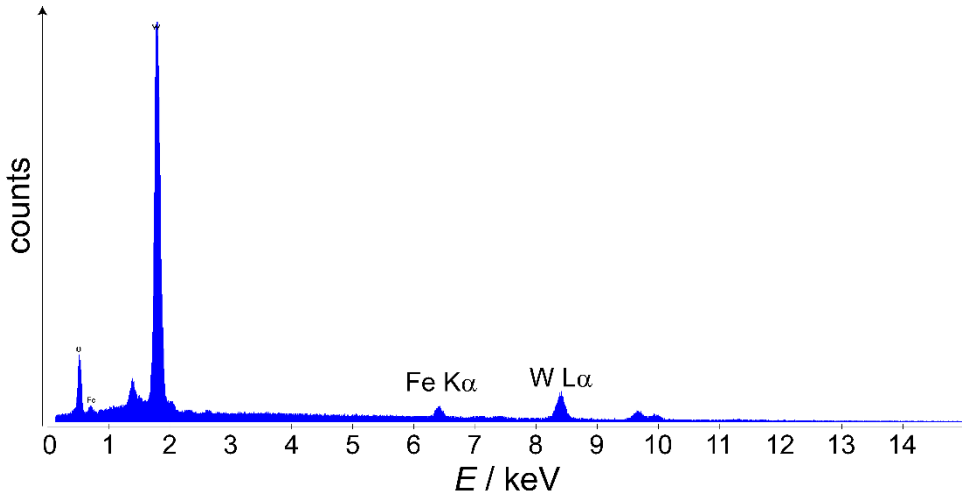

Fig. S5. EDX spectrum of a WO_3-FeOOH electrode.

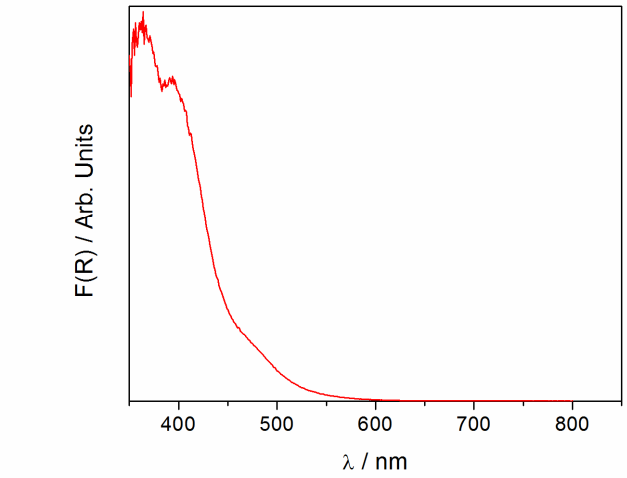

Fig. S6. F(R) spectrum for FeOOH electrochemically grown onto FTO.

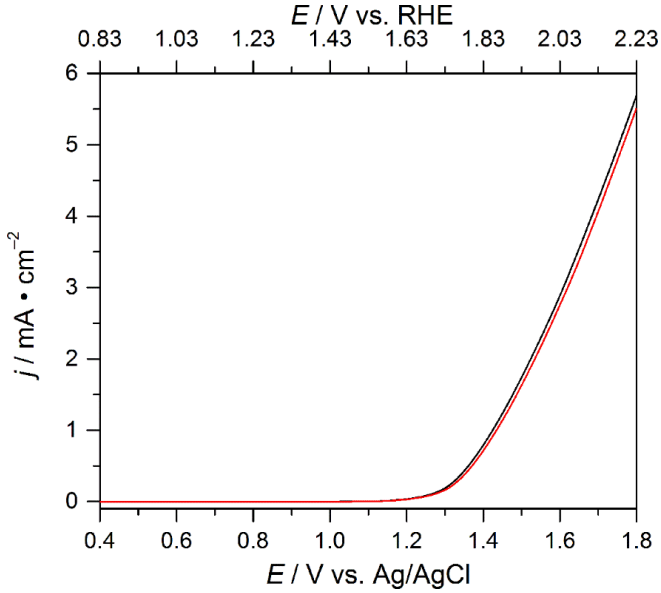

Fig. S7. LSV traces of FeOOH recorded in the dark (red) and under chopped light illumination (black).

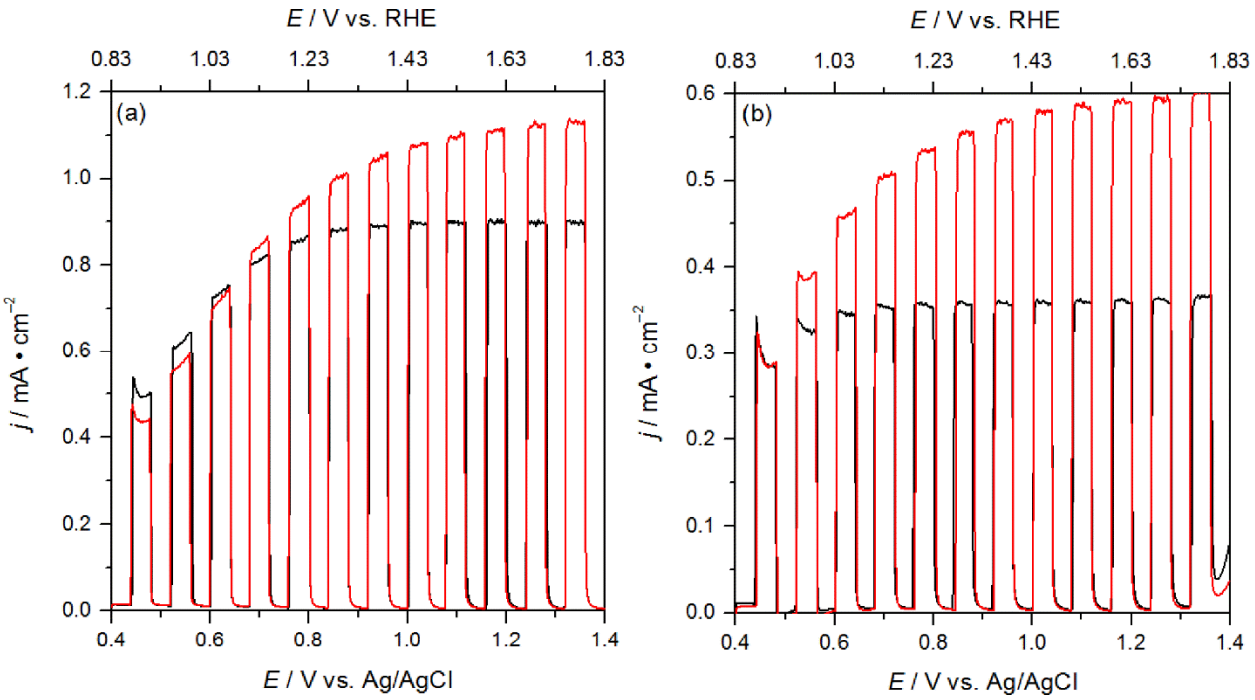

Fig. S8. CL-LSVs for a) WO_3 and b) FeOOH recorded in 0.1 M KP_i buffer at pH 4 under 100 mW/cm^2 AM1.5G illumination. The sweep rate is 20 mV/s. Data in black represent voltammograms recorded under front-side illumination, and data in red under back-side illumination.

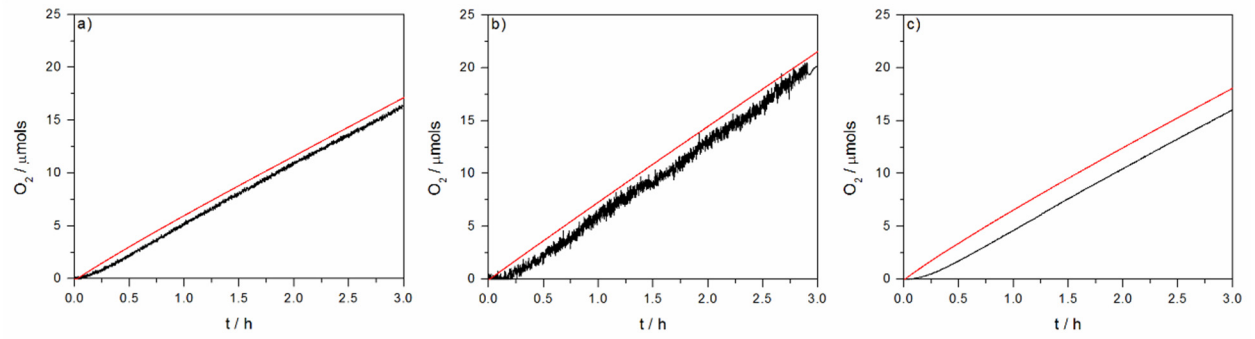

Fig. S9. Three trials of oxygen-evolution Faradaic efficiency measurements on WO_3-FeOOH recorded at 1.43 V vs. RHE in 0.1 M KP_i buffer at pH 4 under 200 mW/cm^2 AM1.5G illumination. The red lines represent the theoretical yield of O_2 based on the charge passed, and the black lines indicate the O_2 measured by the Neofox O_2 fluorescence probe. For each experiment, a fresh WO_3-FeOOH electrode was employed. From left to right, the Faradaic efficiencies are 95.6, 97.7, and 94.5% respectively.

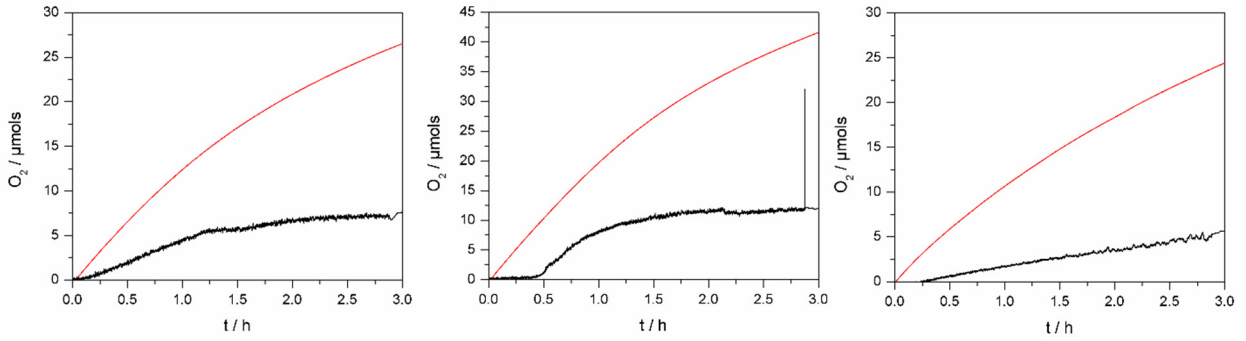

Fig. S10. Three trials of oxygen-evolution Faradaic efficiency measurements on WO_3 recorded at 1.43 V vs. RHE in 0.1 M KP_i buffer at pH 4 under 200 mW/cm^2 AM1.5G illumination. The red lines represent the theoretical yield of O_2 based on the charge passed, and the black lines indicate the O_2 measured by the Neofox O_2 fluorescence probe. For each experiment, a fresh WO_3 electrode was employed. From left to right, the Faradaic efficiencies are 28.7, 28.8, and 23.1% respectively.

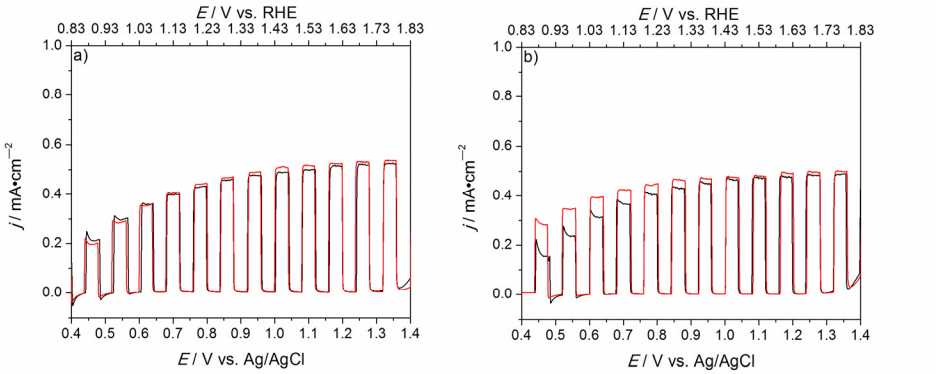

Fig. S11. CL-LSVs of a WO_3-FeOOH electrode before (black) and after (red) having been soaked overnight in a) 0.1M pH 4 KPi and b) 0.1M pH 7 KPi solutions. CL-LSVs were collected in 0.1M pH 4 KPi under 1 sun illumination at 20 mV/s.

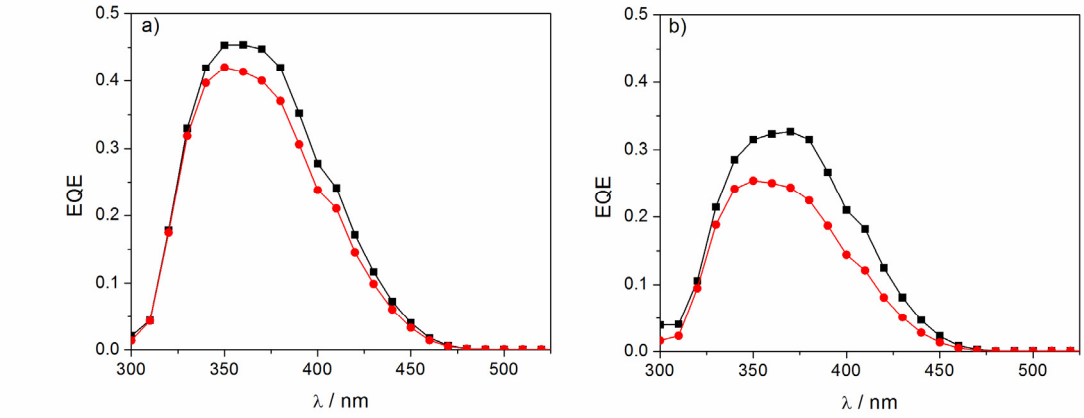

Fig. S12. EQE at different light chopping frequencies of a single WO_3 film before (a) and after (b) loading the FeOOH OEC. Black lines represent the EQE at 15Hz and red represent the EQE at 20 Hz.

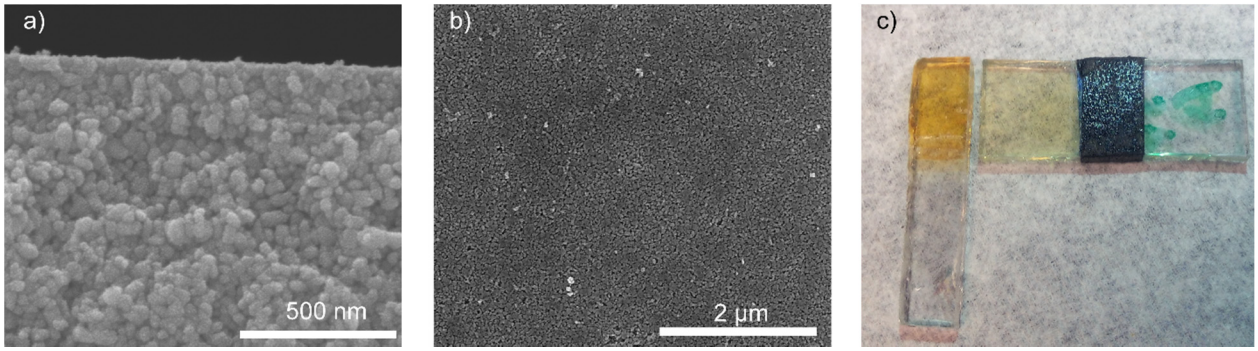

Fig. S13. 1) Cross-sectional SEM image of a WO_3-FeOOH electrode; b) top-down SEM image, and c) photograph of the electrode. For c), the electrode on the left is the sample used for SEM imaging and the electrode on the right is a WO_3 film for comparison. No additional layer is visible in the cross-sectional SEM image, indicating that the FeOOH may grow primarily in the interstices of the film.

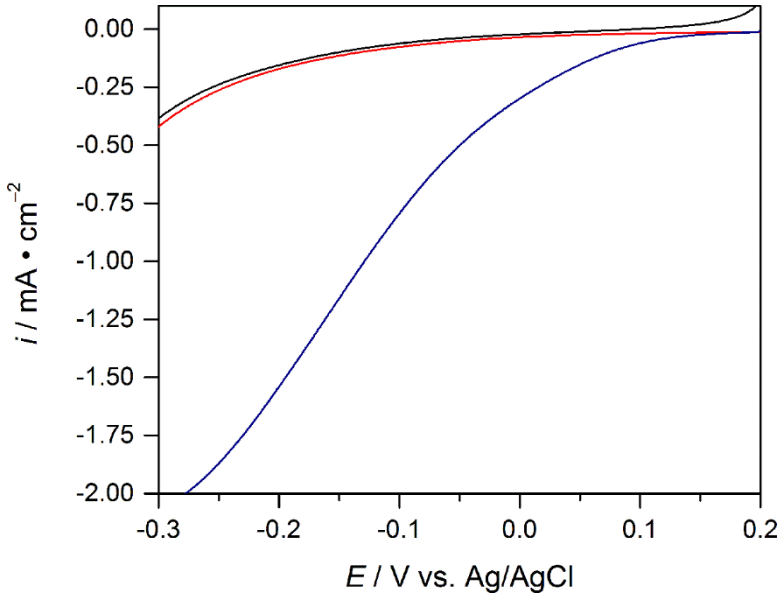

Fig. S14. Electrochemical detection of H_2O_2 on WO_3. Cathodic LSV scans were recorded before (black) and after (red) CPC of a WO_3 electrode under 1-sun AM1.5G illumination at 1.23 V vs. RHE for 2 hours in a 0.1 M KP_i buffer at pH 4. The blue line represents the cathodic scan of a WO_3 electrode in an identical solution that was spiked with 10 µL of H_2O_2.

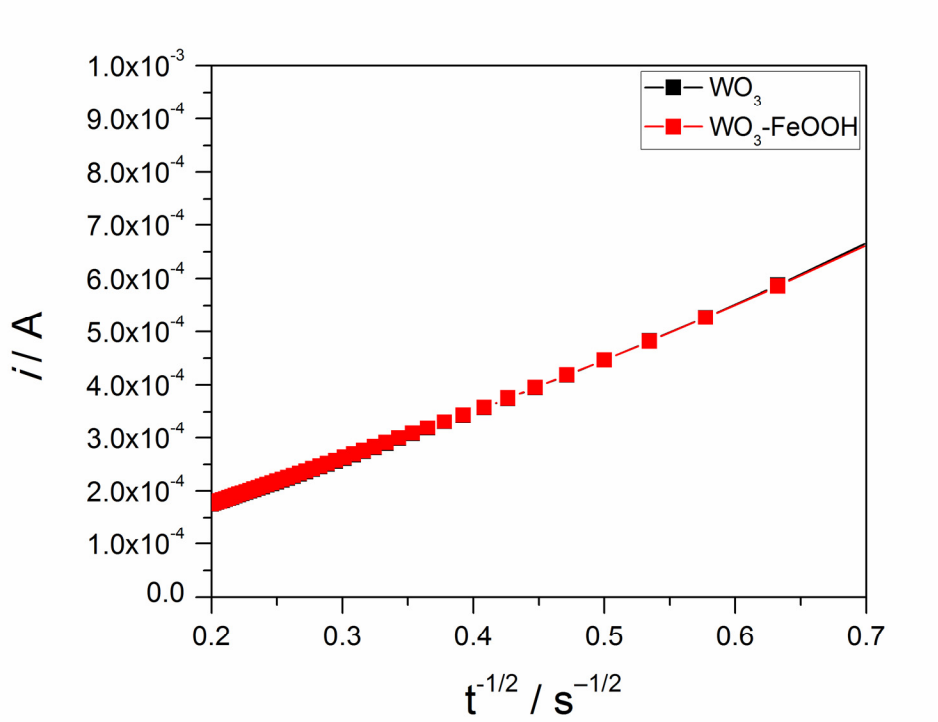

Fig. S15. Cottrell plot of the amperometric *i*-*t* curve. $[Fe(CN)_6]^{3-}$ reduction was measured at –0.05 V vs. Ag/AgCl in a 0.1 M KCl solution containing 6 mM $K_3[Fe(CN)_6]$. The Cottrell equation predicts a linear change in *i* vs. $t^{-1/2}$ and the slope is proportional to the active surface area of the electrode.

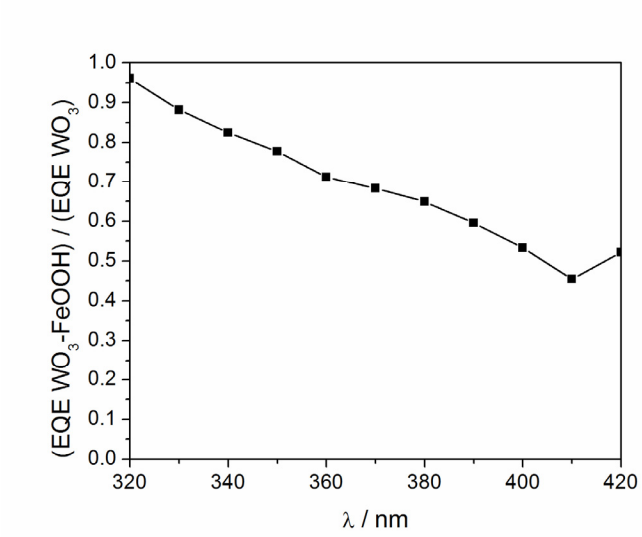

Fig. S16. (EQE WO_3) / (EQE WO_3-FeOOH). This plot was constructed from the data represented in Fig. 7 of the manuscript by taking the EQE of WO_3-FeOOH and dividing it by the EQE of WO_3. A decrease in (EQE WO_3-FeOOH) / (EQE WO_3) is observed with increasing λ due to parasitic absorption from the FeOOH.