Electronic Supplementary Material (ESI) for Energy & Environmental Science.

Supporting Information for:

Mechanistic Insights into Solar Water Oxidation by Cobalt-Phosphate-Modified α-Fe_2O_3 Photoanodes

Gerard M. Carroll, Diane K. Zhong, Daniel R. Gamelin*

E-mail: *Gamelin@chem.washington.edu*

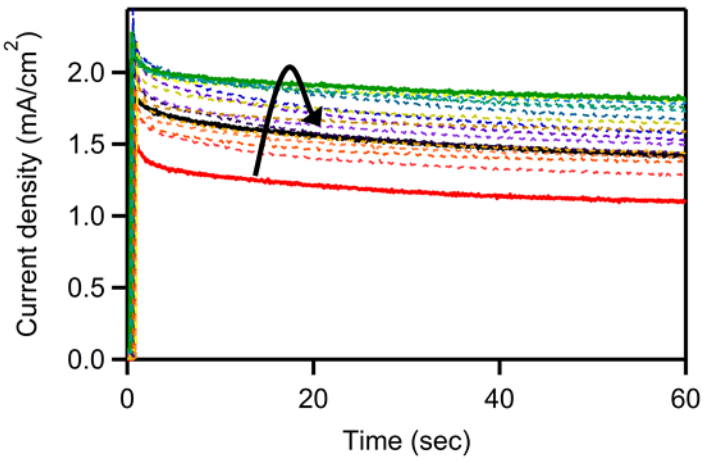

Figure S1. Steady state photocurrent density under simulated 1 sun AM 1.5 back-side illumination of a bare hematite electrode (black) and following Co-Pi deposition (red, 24.5 nm thick) at 1.7V vs RHE. Intermediate colors from orange to blue show the *J-V* scans of the same electrode after |1|3|5|10|15|20|30|40|50|60|120|240|360|480|600 minutes of Co-Pi dissolution in fresh 0.1M KPi pH 8 electrolyte solution. Steady state dark current has been subtracted from the data.

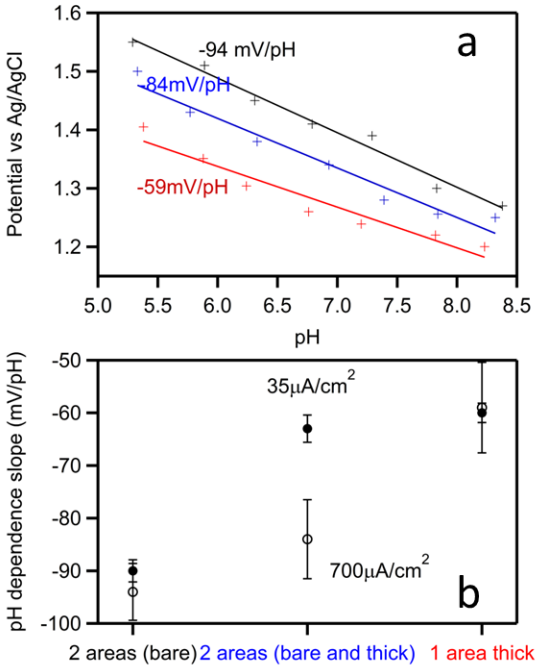

Figure S2. (a) Galvanostatic titration of double spot experiment at 700μA/cm^2 showing two bare spots (black), only the Co-Pi covered spot (red) and both the bare and Co-Pi coated spots measured simultaneously (blue). **(b)** Plot of the slopes from the linear regression of the pH dependence data for: 700 μA/cm^2 (open circle), and 35 μA/cm^2 (closed circle). The error bars indicate the error to the fits.

Figure S2 shows the results from a double spot experiment in which two areas on the same photoanode were masked separately. By partitioning the sample into two spots, Co-Pi could be selectively deposited onto one and not the other, and the pH dependence of both spots measured separately or simultaneously. From Figure S2b, when both spots are bare, the pH dependence is consistent with that of the data presented in Figure 5 (main text). When Co-Pi is deposited onto the surface of only one of the spots, the pH dependence for the current density 30μA/cm^2 increase from -90mV/pH to -62mV/pH, and for a current density of 700μA/cm^2 the slope changes from -94mV/pH to -85mV/pH. When only the spot with Co-Pi is measured, the slopes for 30 and 700μA/cm^2 are -60 and -59mV/pH, respectively. Following the pH measurements, the region with no deposited Co-Pi was investigated with EDX measurements, and no cobalt was detected. This result indicates that an intermediate pH dependence slope is consistent with two simultaneous water oxidation mechanisms.