Supporting Information

Photo-Assisted Electrodeposition of Cobalt-Phosphate (Co-Pi) Catalyst on Hematite Photoanodes for Solar Water Oxidation

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Figure S1. a) SEM image of a Co-Pi/α-Fe₂O₃ photoanode prepared by photo-assisted electrodeposition of Co-Pi. (b) Map of the Co(K) signal intensity in the area depicted in panel (a). (c) The single nodule (of a Co-Pi/α-Fe₂O₃ film prepared by photo-assisted electrodeposition) used in the EDX analysis of Fig. 2b. The nodule is marked with a red box.

Figure S2. Time dependence of the photocurrent density of a Co-Pi/α-Fe₂O₃ photoanode prepared by photo-assisted electrodeposition, measured at 1.0 V vs RHE in 1 M NaOH under continuous 1 sun, AM 1.5 simulated solar irradiation. The electrolyte was not stirred. The electrolyte was replaced after 75 hrs (dashed line), resulting in recovery of photocurrent density.
Figure S3. Average cathodic shifts plotted vs average onset potentials for Co-Pi/α-Fe₂O₃ photoanodes prepared by photo-assisted electrodeposition (P-Dep) and electrodeposition (E-dep) of Co-Pi, and for Co²⁺/α-Fe₂O₃ photoanodes prepared by surface adsorption of Co²⁺ (Co-dip) for the 12 films of Figure 5. Error bars indicate standard deviations. The open symbols represent the parent α-Fe₂O₃ photoanodes. These data show a strong correlation between the two performance metrics, with photo-assisted electrodeposition of Co-Pi leading to the lowest onset potentials and the greatest cathodic shifts.

Figure S4. Average photocurrent density increase vs photocurrent at 1.1 V vs RHE (one-sun) for the 12 films of Figure 5. Photo-assisted electrodeposition of Co-Pi yields the largest photocurrent density increases and the highest absolute photocurrent densities. Error bars indicate standard deviations. The open symbols represent the parent α-Fe₂O₃ photoanodes.
Figure S5. The IPCE (solid colored curves) at 1.23 and 1.43 V vs RHE of a Co-Pi/α-Fe₂O₃ photoanode prepared by photo-assisted electrodeposition are shown with the solar photon flux (AM 1.5G, 100 mW/cm²) as a function of wavelength. Multiplication of the IPCE and the solar photon flux give the shaded areas, which are integrated with respect to the wavelength to give the predicted solar photocurrents (broken colored curves) of 2.9 and 3.4 mA/cm² at 1.23 and 1.43 V vs RHE, respectively.