

Energy & Environmental Science

Accepted Manuscript



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Mechanistic Insights into Solar Water Oxidation by Cobalt-Phosphate-Modified α -Fe₂O₃ Photoanodes

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Abstract: Interfacing α -Fe₂O₃ photoanodes with the water-oxidation electrocatalyst Co-Pi is known to enhance their photon-to-current conversion efficiencies by reducing electron-hole recombination near their surfaces, particularly at more negative potentials, but the mechanism by which Co-Pi modification achieves this enhancement remains poorly understood. Conflicting experimental observations have been recorded with respect to the role of Co-Pi thickness and even the participation of Co-Pi in catalysis, raising important general questions concerning the fundamental properties of catalyst-modified PEC water-oxidation photoanodes for solar energy conversion. Here, we report results from electrochemical, spectroscopic, and microscopic measurements on mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes that reveal evolving pathways of water oxidation with increasing Co-Pi thickness. These results highlight major fundamental differences between structured and planar Co-Pi/ α -Fe₂O₃ composite photoanodes and help to reconcile previously conflicting mechanistic interpretations.

Introduction

Photoelectrochemical (PEC) water splitting into hydrogen and oxygen is a promising strategy for capturing and storing the abundant solar energy incident upon the Earth's surface.¹⁻⁶ Photoelectrolysis of water poses significant technical challenges, however. The oxidation half reaction is a four-proton, four-electron process that typically requires a large overpotential.¹⁻⁶ Additionally, PEC photoelectrodes must be efficient, stable under operating conditions, able to absorb a large fraction of the visible spectrum, possess properly aligned band edges for thermodynamically favorable charge transfer, and be cost effective.^{4, 5, 7} To date, no single material has demonstrated all of these characteristics.

With a band gap of 2.1 eV, stability under operating conditions, and a valence-band potential \sim 1.6 V more positive than the thermodynamic water-oxidation potential (+1.23 V vs RHE), hematite (α -Fe₂O₃) continues to attract attention as a model photoanode for PEC water oxidation.⁷⁻¹¹ Owing to poor charge mobility (10^{-2} to 10^{-1} cm²s⁻¹V⁻¹),¹² short hole-diffusion lengths (2-20 nm),^{13, 14} and slow charge-transfer kinetics (10^{-3} sec to 1 sec),¹⁵⁻²² however, the solar-to-hydrogen efficiencies achieved with α -Fe₂O₃ photoelectrodes suffer greatly from electron-hole recombination, both within the bulk and at the semiconductor liquid junction (SCLJ).

Several strategies have been explored to reduce bulk electron-hole recombination in α -Fe₂O₃, including doping with Si, Ti, Al, Ge, Sn, and Nb²³⁻²⁸ and nano-structuring.^{9, 23-26, 29-33} Similarly, several groups have explored interfacing α -Fe₂O₃ with water-oxidation catalysts to reduce surface electron-hole recombination.^{8, 15, 34-36} In particular, the earth-abundant, self-healing water-oxidation electrocatalyst known as cobalt phosphate (Co-Pi)^{37, 38} has received enormous attention since initial observations of water-oxidation onsets shifted to more negative potentials in Co-Pi/ α -Fe₂O₃ composite photoanodes.^{8, 34, 39} As a "self-healing" catalyst,³⁸ Co-Pi has practical advantages over other molecular or nanocrystalline catalysts, which may degrade or dissociate from the photoanode surface over time.

Since first reported,³⁴ numerous studies have addressed optimization and mechanistic probing of the Co-Pi/ α -Fe₂O₃ interface.^{8, 15, 39-42} Interestingly, these studies have generated seemingly incompatible models to explain the nature of the Co-Pi photocurrent enhancement on α -Fe₂O₃ photoanodes. For example, some of the most detailed insights into this interface have come from studies of planar Co-Pi/ α -Fe₂O₃ "model" systems⁴¹ but the experimental results from these model systems haven't been in full agreement with those from PEC studies of high-surface-area Co-Pi/ α -Fe₂O₃ composite photoanodes.^{8, 39} Specifically, photoelectrochemical measurements on mesostructured α -Fe₂O₃ photoanodes have

indicated an optimal Co-Pi thickness of only $< \sim 10$ nm, beyond which the PEC performance actually diminished because of a "kinetic bottleneck".^{8, 39} In contrast, analogous PEC measurements on planar α -Fe₂O₃ photoanodes have showed continued PEC improvement with increasing Co-Pi thickness up to as thick as 425 nm.⁴¹ One hypothesis⁴¹ to explain these contradictory observations is that the latter measurements involved backside illumination (*i.e.*, through the substrate and α -Fe₂O₃, Figure 2a), whereas the former involved frontside illumination (*i.e.*, through the Co-Pi); Frontside illumination is potentially subject to parasitic photon absorption by the Co-Pi itself,⁴³ introducing new absorption losses with increasing Co-Pi thickness. This hypothesis has never been tested, and the stark contrast between mesostructured and planar Co-Pi/ α -Fe₂O₃ composite photoanodes thus remains unexplained. Additionally, transient absorption measurements on mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes have revealed photogenerated holes with extended lifetimes apparently within the α -Fe₂O₃ itself, leading to the suggestion that Co-Pi does not directly participate in water-oxidation catalysis but instead plays an indirect role by inducing additional α -Fe₂O₃ band bending that reduces electron-hole recombination.^{40, 44} This suggestion appears incompatible with observations of an "adaptive junction" formed between α -Fe₂O₃ and Co-Pi or related catalysts,^{42, 45} and of capacitive hole storage within the Co-Pi layer.⁴¹ These mechanistic contrasts also remain unresolved. Further mechanistic studies of PEC water oxidation by Co-Pi/ α -Fe₂O₃ composite photoanodes are required to reconcile these divergent understandings of this important interface.

Here, we assess the influence of Co-Pi layer thickness on the PEC performance of mesostructured α -Fe₂O₃ photoanodes with the aim of consolidating the understanding of the role of Co-Pi in enhancing PEC water oxidation by α -Fe₂O₃ photoanodes. The results demonstrate the existence of an optimal Co-Pi thickness that is rather small (~ 2.5 nm, estimated from Coulometry) and independent of the illumination direction, confirming a non-trivial origin of the diminished PEC performance with thicker Co-Pi catalyst layers. This bottleneck with thick Co-Pi layers is proposed to stem from the texturing of these mesostructured α -Fe₂O₃ photoanodes, which enhances surface electron-hole recombination relative to planar α -Fe₂O₃ photoanodes. Furthermore, mechanistic insights gained from measuring the pH dependence of this PEC activity as a function of Co-Pi thickness reveal that at large Co-Pi thicknesses, all water oxidation proceeds via Co-Pi, whereas at the optimal Co-Pi thickness, charge transfer to water occurs through Co-Pi-catalyzed water oxidation *and* by direct α -Fe₂O₃ water oxidation, the relative importance of each pathway changing with applied potential. These findings shed new light on the role Co-Pi plays in improving the performance of these and related solar water-splitting photoanodes, and highlight fundamentally important contrasts between planar and structured composite photoanodes.

Experimental

Mesostructured α -Fe₂O₃ photoanodes were fabricated on fluorine doped tin oxide (FTO) coated glass (TEC 15, Hartford Glass Co.) by an atmospheric pressure chemical vapor deposition (APCVD) method described previously.^{8, 33, 39} The APCVD synthesis was modified to optimize α -Fe₂O₃ for backside illumination photocurrent densities by decreasing the deposition period to $\sim 70\%$ of the typical deposition time, and thus producing thinner α -Fe₂O₃ films. To fabricate the Co-Pi/ α -Fe₂O₃ composite photoanodes, Co-Pi was deposited onto α -Fe₂O₃ photoanodes by photo-assisted electrodeposition under AM1.5 simulated solar irradiation from the back of the sample (through the FTO). All Co-Pi depositions were carried out at a constant current of 6 $\mu\text{A}/\text{cm}^2$ from a solution of 0.5 mM cobalt nitrate in 0.1 M potassium phosphate buffer at pH 8. The Co-Pi thickness was controlled by varying the amount charge passed, *i.e.*, the duration of deposition. Co-Pi thicknesses are reported as the average values estimated from the charges passed during deposition. Co-Pi dissolution was achieved by submerging Co-Pi/ α -Fe₂O₃ composite photoanodes in fresh aqueous 0.1M KPi (pH 8) solutions for fixed times.

Photoelectrochemical (PEC) and electrochemical (EC) measurements were conducted in a three-electrode configuration, with the photoanode as the working electrode, Ag/AgCl as the reference electrode, and Pt as the counter electrode. A Gamry Series G 300 potentiostat with a frequency response analyzer was used for all measurements. Unless otherwise stated, all PEC measurements were performed in 0.1M KPi (pH8) using backside illumination (through the FTO, Figure 2a) with calibrated 1 sun AM 1.5 simulated sunlight irradiation using an Oriel 96000 solar simulator equipped with a 150 W Xenon arc lamp and an Oriel AM 1.5 filter. Potentials vs the reversible hydrogen electrode (RHE) were calculated using the Nernst equation as $E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591(\text{pH}) + 0.1976$ V. All photocurrent-voltage and current-voltage data were collected at a scan rate of 10 mV/s. Masks with 6 mm diameter apertures were applied onto all working electrodes for defined active surface areas.

Galvanostatic pH-dependent PEC measurements were performed by titrating aqueous 0.5M KPi (pH 5) with aqueous 0.1M KOH. Incident photon-to-current conversion efficiency (IPCE) data were collected using a 250 W tungsten light source directed through an Oriel Cornerstone 74000 monochromator blazed at 350 nm. Spectral efficiency was calculated using the equation: $\text{IPCE}(\lambda) = 1240 \cdot \text{Current}(\text{A}) / \text{Power}(\text{W}) \cdot \lambda(\text{nm})$. Light intensity was measured with a calibrated silicon detector with a maximum light output of ~ 6 mW/cm² at 540 nm. The steady-state dark current was collected prior to each IPCE measurement and was subtracted from the resulting spectrum. Scanning electron microscopy (SEM) images were collected using an FEI Sirion SEM at an accelerating voltage of 15 keV.

Results and Analysis

Figure 1 compares scanning electron microscopy (SEM) images of an α -Fe₂O₃ photoanode collected before and after photo-assisted electrochemical deposition of Co-Pi with backside illumination. Whereas photo-assisted electrochemical deposition of Co-Pi onto α -Fe₂O₃ mesostructures using frontside illumination has previously been shown to yield uniform catalyst coverage across the entire α -Fe₂O₃ surface,⁸ Co-Pi deposition via backside illumination has not been explored. The bare α -Fe₂O₃ photoanode displays a highly structured surface with resolvable features on the order of ~10 nm in diameter, typical for mesostructured α -Fe₂O₃ photoanodes prepared by APCVD.³³ Following Co-Pi deposition, the smallest resolvable features grow to ~30 nm. Assuming an average volume of ~125 Å³ per CoO₆ subunit,⁴⁶ and an α -Fe₂O₃ surface roughness factor of 20,³³ an average Co-Pi thickness of ~25 nm can be estimated from the charge passed during deposition to make the composite photoanode in Figure 1b. Although it is difficult to extract the exact Co-Pi thickness from SEM, the loss of resolvable microstructure in Figure 1b is consistent with this estimated thickness.

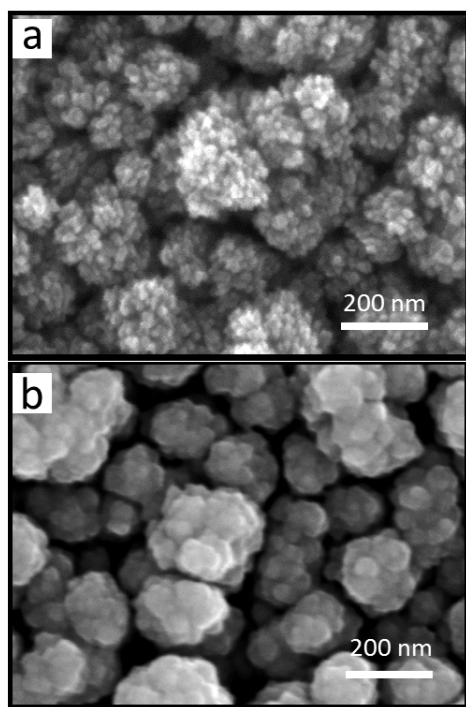


Figure 1. Scanning electron microscope images of (a) a bare mesostructured α -Fe₂O₃ photoanode, and (b) the same photoanode following deposition of a ~25 nm thick layer of Co-Pi via photo-assisted electrochemical deposition using backside illumination. The viewing angle is normal to the sample surface.

Figure 2b describes the photocurrent density–voltage (J - V) characteristics of an α -Fe₂O₃ photoanode whose surface has been modified by deposition of a thick (~25 nm) layer of Co-Pi,

illuminated with 1 sun, AM1.5 simulated sunlight from the back side. Remarkably, the onset potential for PEC water oxidation is approximately the same with and without the thick Co-Pi layer. The photocurrent density measured at +1.8 V is greater for the Co-Pi/ α -Fe₂O₃ photoanode than for the parent α -Fe₂O₃ photoanode, but close inspection reveals that this enhancement arises from direct electrocatalysis by Co-Pi (Fig. 2b, inset), instead of from enhanced photoelectrocatalysis as desired. Subtracting the steady state dark current yields a photocurrent density of only 1.2 mA/cm² at +1.8 V for the composite photoanode, well below that of the parent α -Fe₂O₃ photoanode (1.5 mA/cm² at +1.8 V). Interfacing with a ~25 nm Co-Pi layer thus actually diminishes the PEC performance of mesostructured α -Fe₂O₃ photoanodes under backside illumination, confirming previous observations of a kinetic bottleneck in this regime.

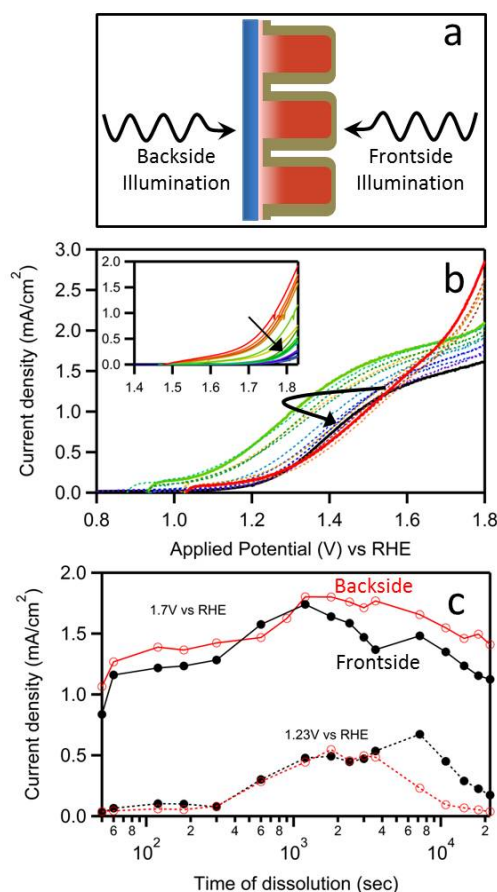


Figure 2. (a) Schematic illustration of front- and backside illumination. (b) J - V scans under simulated 1 sun AM 1.5 backside illumination of a bare α -Fe₂O₃ electrode (black) and following Co-Pi deposition (red, ~25 nm thick). Intermediate colors from orange to blue show the J - V scans of the same 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. The solid lines correspond to minima (bare α -Fe₂O₃, and with ~25 nm-thick Co-Pi) and the maximum (after 30 min dissolution). Inset: Dark current response of the same anode at each of the same stages of Co-Pi dissolution. (c) Steady-state photocurrent densities (steady-state dark current subtracted) for front (black, closed circles) and backside (red, open circles) illumination measured at +1.7 V (solid) and +1.23 V (dashed) vs RHE. All data were collected using 0.1M KPi (pH 8) buffer.

Co-Pi slowly disproportionates and dissolves in cobalt-free electrolyte under open-circuit conditions.³⁸ Here, we show that this dissolution can be used to optimize the Co-Pi thickness in Co-Pi/ α -Fe₂O₃ composite photoanodes. To illustrate this optimization, a series of PEC measurements was performed on the same photoanode in cobalt-free electrolyte, with deliberate Co-Pi dissolution steps performed between each pair of J - V measurements. Specifically, the composite photoelectrode was transferred to a cobalt-free aqueous solution following each PEC measurement, where dissolution was allowed to proceed for a fixed time, and the photoelectrode was then transferred back into the PEC cell and its J - V response measured again. From the initial thickness of \sim 25 nm (red trace), Figure 2b shows that the onset potential shifts to more *negative* potentials with Co-Pi dissolution until a maximum shift is reached at \sim 30 min dissolution time (green trace). Further dissolution then shifts the onset potential to more positive potentials again, until eventually all of the Co-Pi has been removed and the J - V curve converges on that of the parent α -Fe₂O₃ photoanode, measured prior to any Co-Pi deposition. From the inset in Figure 2b, the dark current density does not follow the same trend; its onset potential only increases with Co-Pi dissolution. Figure 2c summarizes steady-state photocurrent density data (see Supporting Information) measured with both front- and backside illumination at +1.7 V and +1.23 V as a function of Co-Pi dissolution time. Both the front- and backside PEC follow the same trend, proceeding through a maximum at \sim 30 min dissolution. This trend illustrates the "kinetic bottleneck" effect described previously,³⁹ but here is demonstrated with backside illumination. This result eliminates nonproductive photon absorption by Co-Pi as a viable hypothesis to explain the reduced PEC performance of composite Co-Pi/ α -Fe₂O₃ photoanodes having thick Co-Pi layers.

Figure 3 shows incident-photon-to-current-conversion-efficiency (IPCE) curves measured for the same α -Fe₂O₃ photoanode with various Co-Pi thicknesses. The bare α -Fe₂O₃ photoanode shows a typical response, with its photocurrent onset at the α -Fe₂O₃ absorption edge ($\lambda \approx$ 600 nm) and a maximum of 14% at $\lambda =$ 450 nm. The decreasing IPCE at even shorter wavelengths is typical for backside illumination, and reflects bulk-recombination losses of photo-generated charge carriers created near the α -Fe₂O₃/FTO interface. Deposition of a thin Co-Pi layer (\sim 2.3 nm) onto this photoanode's surface increases the IPCE values at all wavelengths, yielding a maximum of \sim 19% at 445 nm. Addition of more Co-Pi (to \sim 9.7 nm thick) causes a decrease in IPCE throughout the entire spectral window, however, and the IPCE curve is almost indistinguishable from that of the bare photoanode. Even further Co-Pi addition (to \sim 25 nm) decreases the IPCE values yet further, yielding an IPCE maximum of only 7% at $\lambda =$ 445 nm. The uniform decrease in IPCE with thick Co-Pi deposition differs from what would be expected if this large reduction in PEC performance came from photon absorption by Co-Pi (dotted curve, transmittance), further arguing against the hypothesis of substantial non-productive light absorption by the catalyst. Instead, the results presented here indicate that a more

complex and fundamentally important limitation is encountered with thick Co-Pi layers.

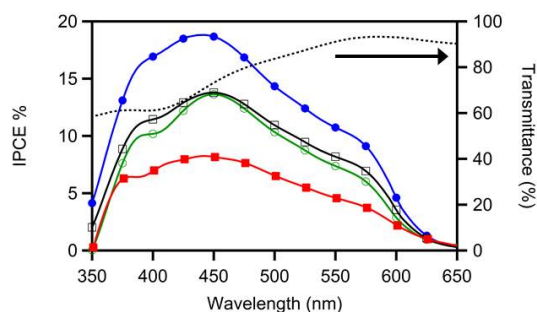


Figure 3. Incident photon to current conversion efficiency (IPCE) spectra for bare (black, open square), 2.3 nm (blue, closed circle), 9.7 nm (green, open circle) and 25 nm (red, closed square) thick Co-Pi on α -Fe₂O₃ in 0.1 M KPi at 1.7 V vs. RHE from backside illumination. For reference, the dashed line shows the transmittance spectrum of a \sim 25 nm thick Co-Pi layer deposited on FTO.

In our experiments, the optimized thicknesses of the APCVD α -Fe₂O₃ photoanodes themselves for front- and backside illumination are \sim 600 and \sim 450 nm, respectively. Figure 4 shows J - V curves measured for two Co-Pi/ α -Fe₂O₃ composite photoelectrodes, with α -Fe₂O₃ growth optimized for either front (\sim 600 nm thick) or backside (\sim 450 nm thick) illumination. Figure 4a shows that the thicker α -Fe₂O₃ photoanode achieves a lower plateau current density (\sim 1 mA/cm²) than the thinner one (\sim 2 mA/cm²) under backside illumination. Upon deposition of \sim 25 nm (average) Co-Pi onto these two photoanodes, the photocurrent onset potential of the thicker photoanode shifts to more *negative* potentials by \sim 200 mV, whereas that of the thinner photoanode actually shifts to more *positive* potentials. A close inspection of the SEM image of this Co-Pi/ α -Fe₂O₃ photoelectrode (Figure 4a, inset) reveals that backside photo-assisted electrodeposition does not uniformly deposit Co-Pi onto the surface of the thicker α -Fe₂O₃ photoanode. The nodules still show their fine microstructure whereas the dark regions in the valleys now appear flat, suggesting that Co-Pi deposits preferentially in the valleys. This result implies that the PEC activity of the thicker α -Fe₂O₃ photoanode is restricted to these valleys when using backside illumination, and the high-surface-area nodules do not participate equally. This loss of active surface area causes the thicker α -Fe₂O₃ photoelectrodes to behave like planar α -Fe₂O₃ photoanodes when interfaced with Co-Pi, showing continued shifting to more negative potentials of the onset potential even with application of thick Co-Pi layers (Figure 4a).⁴¹ In contrast, the thinner α -Fe₂O₃ photoanode shows evidence of substantial Co-Pi deposition onto the high-surface-area nodules (Figure 4b, inset) even with backside illumination, showing that the full surface area participates in water oxidation, as desired. In this limit, thick Co-Pi layers impair PEC performance (Figure 4b).

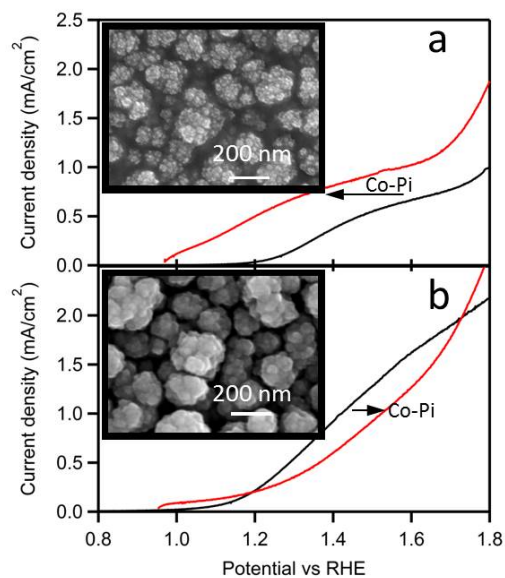


Figure 4. *J-V* scans for bare (black) and ~ 25 nm Co-Pi-coated (red) α -Fe₂O₃ photoanodes measured in 0.1 M KPi (pH 8) with backside illumination. **(a)** Co-Pi/ α -Fe₂O₃ optimized for frontside illumination (~ 600 nm thick α -Fe₂O₃). **(b)** Co-Pi/ α -Fe₂O₃ optimized for backside illumination (~ 450 nm thick α -Fe₂O₃). The insets show SEM images of the two Co-Pi/ α -Fe₂O₃ photoelectrodes.

We now turn to the water oxidation catalysis itself. To probe this chemistry, galvanostatic pH titrations were conducted under illumination for four different Co-Pi thicknesses at two different current densities on the same 450 nm thick α -Fe₂O₃ photoanode (Fig. 5). As an electrocatalyst, Co-Pi is known to proceed through a proton-coupled electron-transfer step that precedes the rate-limiting O-O bond formation step.⁴⁶ This mechanism yields a Nernstian pH dependence of -59 mV/pH. A pH dependence of ~ -59 mV/pH would therefore be expected for a Co-Pi/ α -Fe₂O₃ composite photoanode if PEC water oxidation proceeds exclusively via the Co-Pi electrocatalyst. For reference, the bare α -Fe₂O₃ photoanode was measured and shows a pH dependence of -97 mV/pH under AM 1.5 illumination from the backside (at both 35 and 700 μ A/cm², Figure 5). Addition of 0.6 nm Co-Pi onto the bare α -Fe₂O₃ photoanode changes the pH dependence from -97 to -82 mV/pH at 35 μ A/cm², and -95 mV/pH at 700 μ A/cm². These changes indicate that Co-Pi is modifying the mechanism of water oxidation in these composite photoanodes, but does so more at low potentials (low currents) than at high potentials (higher currents). Further addition of Co-Pi continues to decrease the pH dependence until, at a Co-Pi thickness of ~ 25 nm, the slopes of both the 35 and 700 μ A/cm² data sets are both close to -59 mV/pH, *i.e.*, both resemble the inverse first order dependence on proton activity anticipated from water-oxidation catalysis by Co-Pi. Co-Pi/ α -Fe₂O₃ composite photoanodes with thick Co-Pi catalyst layers thus appear to oxidize water solely via the Co-Pi electrocatalyst.

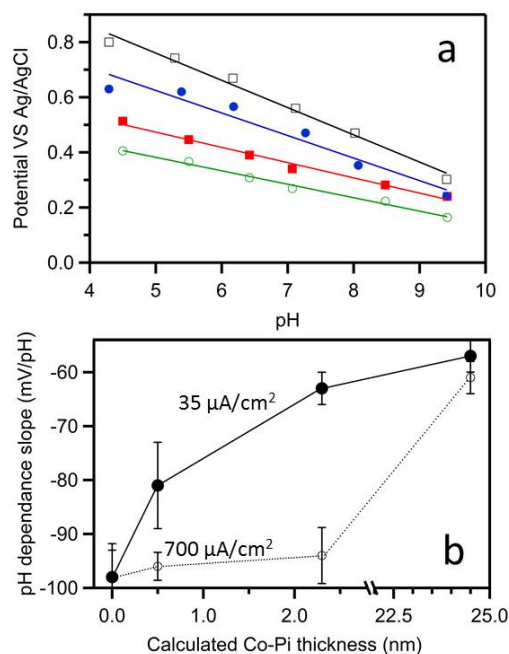


Figure 5. **(a)** Galvanostatic pH titration taken at 35 μ A/cm² of bare α -Fe₂O₃ (black, open square), 0.62 nm Co-Pi/ α -Fe₂O₃ (blue, closed circle), 2.3 nm Co-Pi/ α -Fe₂O₃ (green, open circle) and ~ 25 nm Co-Pi/ α -Fe₂O₃ (red, closed square) in 0.5 M KPi under AM1.5 illumination from the backside. All pH data were collected on the same 450 nm thick α -Fe₂O₃ sample. **(b)** The fitted slopes from the galvanostatic pH titrations at 35 μ A/cm² (closed circles, solid line) and 700 μ A/cm² (open circles, dotted line) plotted vs Co-Pi thickness. Error bars indicate the uncertainty associated with the linear fit to the pH data.

The above data show that Co-Pi/ α -Fe₂O₃ composite photoanodes prepared with the optimized Co-Pi thickness (~ 2.3 nm) exhibit a pH dependence that is intermediate between those of the bare α -Fe₂O₃ and thick-composite photoelectrodes. This intermediate regime is interpreted as reflecting a superposition of two mechanisms (see Supporting Information), one involving water oxidation directly at the α -Fe₂O₃ surface (-97 mV/pH) and the other water oxidation by Co-Pi (-59 mV/pH). The degree to which each mechanism participates varies with current density and hence with applied potential. At low potential (current), the majority of oxygen evolution occurs via Co-Pi, but at higher potentials (currents) the α -Fe₂O₃ surface mechanism dominates. The optimized Co-Pi/ α -Fe₂O₃ composite photoanodes thus rely on Co-Pi catalysis for activity at low potentials and on direct α -Fe₂O₃ water oxidation for activity at high potentials. To our knowledge, this result constitutes the first mechanistic evidence of water oxidation by Co-Pi in such composite photoanodes.

Discussion

Co-Pi can be described as forming an "adaptive Schottky junction"^{42, 45} with the surface of the underlying α -Fe₂O₃ photoelectrode, in which the open circuit voltage and quasi-Fermi level splitting increase upon oxidation of the ion permeable electrocatalyst, increasing the driving force for electron-hole separation and reducing surface recombination. From this description, it is expected that increasing the thickness of Co-Pi should only improve the J - V characteristics of the composite photoelectrode. Such behavior is indeed observed in planar Co-Pi/ α -Fe₂O₃ photoanodes,⁴¹ but it is not observed with mesostructured Co-Pi/ α -Fe₂O₃ photoanodes.^{8, 39} Although mesostructured α -Fe₂O₃ photoanodes yield substantially higher photocurrent densities than planar α -Fe₂O₃ photoanodes, the PEC performance of mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes maximizes at an intermediate Co-Pi thickness, implicating the existence of a new process that limits the overall performance.

We attribute this new limiting process (the "kinetic bottleneck"³⁹) to increased interfacial recombination between conduction-band electrons and Co-Pi holes with increasing Co-Pi layer thickness in the mesostructures, ultimately arising from the inability to sweep electrons away from the SCLJ because of the α -Fe₂O₃ texturing. This interpretation is summarized in Figure 6a. Electron diffusion in a planar α -Fe₂O₃ photoanode is largely perpendicular to (away from) the SCLJ (Figure 6a, left). Increasing the surface area of an α -Fe₂O₃ photoanode increases the distance that photogenerated electrons must travel before they are no longer in proximity to this interface. Much of this added distance is actually parallel to the SCLJ (Figure 6a, right). The probability of electron recombination with holes stored within the Co-Pi layer increases in proportion to the time

the electrons must reside near the SCLJ. This contrast results in the existence of the kinetic bottleneck only in highly structured Co-Pi/ α -Fe₂O₃ composite photoanodes, and only when the entire high surface area participates in the photoelectrocatalysis (Figure 4).

The pH data presented here (Figure 5) indicate that water-oxidation catalysis proceeds exclusively *via* Co-Pi when the Co-Pi layer is thick. Under these conditions, however, many oxidizing equivalents are stored in the Co-Pi layer at steady state, and surface electron-hole recombination in mesostructured photoanodes becomes overwhelmingly problematic. For mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes, PEC performance is therefore optimized when the Co-Pi layer is thin. Interestingly, in these optimized mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes, water-oxidation catalysis proceeds *via* Co-Pi at low potentials but directly *via* the α -Fe₂O₃ surface at high potentials. In this way, Co-Pi improves the performance of mesostructured α -Fe₂O₃ photoanodes by catalyzing water oxidation at the lowest potentials, shifting their onset potentials more negative as desired for practical applications. These conclusions are summarized graphically in Figure 6b and highlight the important fundamental differences between mesostructured and planar PEC photoanodes for solar water oxidation. Importantly, these results shed new light onto the longstanding uncertainty about whether Co-Pi is an active catalyst or merely a spectator in such photoelectrochemistry.⁴⁷ Because of the marked contrasts observed between mesostructured and planar Co-Pi/ α -Fe₂O₃ photoanodes, the results here motivate a more comprehensive mechanistic investigation into the kinetic processes *specific* to mesostructured Co-Pi/ α -Fe₂O₃ interfaces, and such experiments are currently underway in our laboratories.

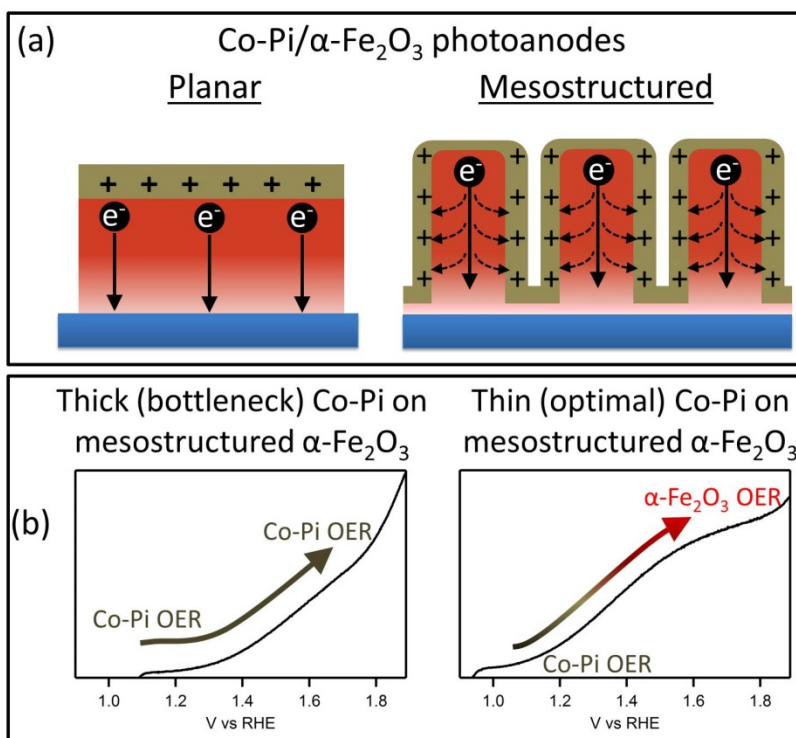


Figure 6. (a) Schematic comparison of contrasting surface electron-hole recombination processes during photoelectrochemical water oxidation by mesostructured and planar Co-Pi/ α -Fe₂O₃ photoanodes. In planar photoanodes, electrons travel away from the SCLJ, and hence away from accumulated holes in the Co-Pi catalyst layer. This configuration minimizes surface electron-hole recombination. In mesostructured photoanodes, electrons spend more time traveling parallel to the SCLJ. When the Co-Pi catalyst layer is thick, it stores many oxidizing equivalents, and thicker Co-Pi deposition results in increased surface electron-hole recombination. (b) In PEC water oxidation by mesostructured Co-Pi/ α -Fe₂O₃ photoanodes, the water-oxidation mechanism depends on the catalyst thickness and the applied potential. For thick Co-Pi catalyst layers, water oxidation is always performed by Co-Pi. For thin (optimized) Co-Pi layers, water oxidation at low potentials is performed by Co-Pi, whereas water oxidation at high potentials and high currents is performed directly by the α -Fe₂O₃ surface.

Conclusion

Highly structured α -Fe₂O₃ photoanodes are susceptible to kinetic constraints when interfaced with thick Co-Pi catalyst layers. Optimization of the Co-Pi electrocatalyst thickness is necessary to achieve the maximum PEC efficiency at potentials $<+1.6$ V vs RHE. Attenuation of photocurrent with increasing Co-Pi thickness arises due to interfacial recombination between photogenerated conduction-band electrons and accumulated Co-Pi holes ("kinetic bottleneck"). The importance of such recombination depends on the texture of the underlying photoanode. For mesostructured α -Fe₂O₃ photoanodes, the overall PEC efficiency is optimized with rather thin Co-Pi layers (~ 2.5 nm) because of this recombination. At these optimal Co-Pi thicknesses, PEC water oxidation can occur from both the Co-Pi electrocatalyst, which dominates at low applied bias, and directly from the α -Fe₂O₃ surface, which dominates at high applied bias. For planar α -Fe₂O₃ photoanodes, this recombination channel is no longer dominant, and very thick Co-Pi layers do not limit PEC performance.⁴¹ These results clarify the mechanistic role that Co-Pi plays in improving the PEC performance of composite Co-Pi/ α -Fe₂O₃ photoanodes,

and may have broad implications with respect to formation and optimization of related composite catalyst/photoelectrodes.

Acknowledgments

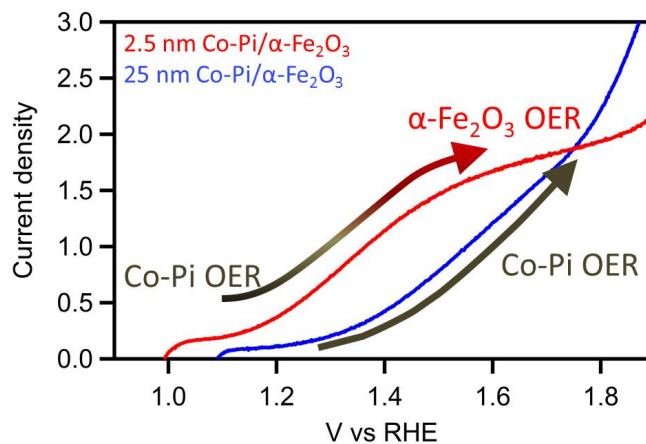
This work was supported by the US National Science Foundation (CHE-1213283) and partially conducted at the UW Nanotechnology User Facility, a member of the NINN.

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TOC Graphic.

20-word description:

Photoelectrochemical measurements on mesostructured Co-Pi/ α -Fe₂O₃ composite photoanodes reveal evolving pathways of water oxidation with increasing Co-Pi thickness and applied bias.