Supplementary information

Extraction of mobile charge carrier photogeneration yield spectrum of ultrathin-film metal oxide photoanodes for solar water splitting

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Extraction of mobile charge carrier photogeneration yield spectrum of ultrathin film

metal oxide photoanodes for solar water splitting

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Supporting Information

Optical spectra and fitting in back illumination



Figure S1. Measured (solid line) and calculated (dashed line) transmittance (T, red), reflectance (R, blue) and absorptance (F_A , green) spectra of 7 nm thick hematite film on ITO coated glass in back illumination in air. The black dotted line is the simulated absorptance in the hematite layer only ($A_{hematite}$).

Analysis of Approximation Error and its Dependence on Sample Thickness

Equation 1 for the EQE in the article is an integral across the thickness *d* of the hematite layer, of the product of two position-dependent terms, the photon flux $I(\lambda, x)$, and the charge carrier collection efficiency p(x), scaled by wavelength-dependent absorption coefficient $\alpha(\lambda)$ and photogeneration yield $\xi(\lambda)$, which is to be solved for. Our solution makes the approximation that, in the ultrathin limit of small *d*, the integral of the product is equal to the product of the spatial averages:

$$\frac{1}{a} \int_0^d I(\lambda, x) p(x) dx \cong \bar{I}(\lambda) \,\bar{p} \tag{S1}$$

where the overbars denote spatial averages over the length. Note that $I_0(\lambda)$, $\alpha(\lambda)$ and $\xi(\lambda)$ from Equation 1 in the article are factored out of the equation for simplicity, as they do not depend on *x*. The accuracy of this approximation will generally depend on the spatial variation of both the intensity and the collection efficiency over the film thickness *d*. In this Supplementary section we evaluate the spatial variations of intensity calculated from our optical model for various thicknesses, and finally compare the left and right hand sides of Equation S1 for those cases to assess the resultant approximation error. We scale both sides of Equation S1 by $\alpha(\lambda)$, so as to replace $I(\lambda, x)$ with the nominal photogeneration profile $G(\lambda, x) = \alpha(\lambda)I(\lambda, x)$ to better represent the actual spectra of interest.

The nominal optical generation profile, plotted against the depth (*x*) into the hematite film and the wavelength (λ) of the incident light, is shown in Figure S2a for a 7 nm thick hematite film.

The incident photon flux was taken to be independent of wavelength. Based on cross-sectional cuts of the $G(\lambda, x)$ profile for each wavelength (λ), the overall spread of intensity, defined by the maximum minus minimum intensity over the entire film thickness, normalized by the mean value $\overline{G}(\lambda)$, is plotted in Figure S2b. As another measure, we calculate the position-dependent deviation of the intensity from the mean value, $G(\lambda, x) - \overline{G}(\lambda)$, and plot the maximum and RMS values in Figure S2b as well. From this figure, we see a small spread of intensities for an ultrathin 7 nm thick film, remaining under 15% over the entire wavelength range.

To assess the errors introduced by this spread in our analysis, we compare the two sides of Equation S1 where p(x) is assumed to take the form of an exponential decay, $p(x) \propto \exp(-x/\ell)$, with a characteristic decay length ℓ . This assumption can be seen to be plausible from the reciprocity theorem for charge carrier collection,¹ where it would follow that ℓ should be comparable to the minority carrier diffusion length. Estimates of the diffusion length in hematite have varied by orders of magnitude in the literature, but to be conservative we use for ℓ one of the lower estimates of 2 nm.² The result is plotted in Figure S2c, showing that for a 7 nm thick film the error introduced by the average approximation is far less than the other errors in the analysis, as described in the article. Averaging this error over the entire wavelength range, the RMS value of ~2% roughly coincides by the average (over wavelength) RMS deviation of intensity from the mean, as can be seen by inspection of Figure S2b.



Figure S2. (a) The nominal photogeneration map, $G(\lambda, x)$, for a 7 nm thick hematite film on ITO coated glass in front illumination. (b) The maximum spread of $G(\lambda, x)$ along the depth, as a function of wavelength (dashed line), and maximum (dotted line) and root-mean-square (solid line) deviations from the mean $\bar{G}(\lambda)$. (c) Comparison of the exact integral $\frac{1}{d} \int_0^d G(\lambda, x) p(x) dx$ with the product-of-means approximation $\bar{G}(\lambda)\bar{p}$, assuming an exponential form of p(x) with characteristic length $\ell = 2$ nm.

The above procedure was repeated for different sample thicknesses of 10 and 20 nm, plotted in Figure S3, which shows increasing deviations. Even for 10 nm, the approximation error is less than 5%, consistent with the average intensity deviation, but for 20 nm thickness some quantitative deviations appear, notably a shift of the ~420 nm peak.



Figure S3. Same analysis as shown in Figure S2 but for 10 nm (a-c) and 20 nm (d-f) thick films. Photogeneration maps $G(\lambda, x)$, for (a) 10 nm thick and (d) 20 nm thick hematite films on ITO coated glass in front illumination: (b),(e) : Maximum spread of $G(\lambda, x)$ along the depth, as a function of wavelength (dashed lines), and maximum (dotted lines) and root-meansquare (solid lines) deviations from the mean $\bar{G}(\lambda)$ for (b) 10 nm and (e) 20 nm films. (c),(f) Comparison of exact integral $\frac{1}{d} \int_0^d G(\lambda, x) p(x) dx$ with the product-of-means approximation $\bar{G}(\lambda)\bar{p}$, assuming an exponential form of p(x) with characteristic decay length $\ell = 2$ nm.

External Quantum Efficiency Measurements and Potential Dependence

This supplementary section evaluates the repeatability, accuracy, light bias conditions, and potential dependence of the external quantum efficiency (EQE) measurements. In Figure S4 (a) we present two sets of measurements on our sample, set #1 and set #2. Set #1 corresponds to the data employed in the article, while set #2 was measured on the same sample nine months later, with identical alignment and measurement procedures, but with a different light bias intensity (as will be described shortly). The "back" illumination cases correspond to the whole sample "cappuccino" cell³ being rotated 180°, with the sample at center of rotation, such that

the monochromatic probe light is incident on the back window of the cell. However, for these "back" measurements, the LED position was also moved so as to continue to shine on the *front* of the sample and LED current adjusted to keep the light bias conditions identical, and produce approximately the same photocurrent.



Figure S4. (a) EQE spectra measured at 1.6 V_{RHE} for front (solid lines) and back (dashed lines) illumination with monochromatic probe light, for the two sets of measurements, #1 (black) and #2 (red) respectively. (b) The bias LED spectra incident on the front surface for all of the measurements in (a), calculated as described in the text. The green curve is the AM 1.5 global tilt solar spectrum. (c) Current-potential curve (solid line) measured along with set #2, for front light bias conditions. The circles are integrations corresponding to Equation S1 based on the LED spectrum measured at sample position for 1000 mA LED current. The inset shows the same, but with the photocurrent plotted on a logarithmic scale. (d) The EQE at each potential, scaled up by the factor indicated in the legend, which was determined from the ratio of the wavelength-averaged EQE's.

As shown in Figure S4(a), the measurements are acceptably repeatable, considering the considerable length of time and difference of light bias between sets #1 and #2. For set #2, the LED position had been moved and consequently the intensity (and photocurrent) was less than half of the original measurement #1. To characterize the light bias spectral intensity at the time

of measurement set #2, an ILT950 spectroradiometer from International Light Technologies, with NIST-traceable calibration, was placed in the sample cell position to measure the spectral power intensity $S_{LED}(\lambda)$ from the LED, whose current was set to 1000 mA. The measured $S_{LED}(\lambda)$ is plotted as a red solid line in Figure S4(c). For comparison, a terrestrial solar irradiance spectrum obtained from the American Society for Testing and Materials (ASTM)⁴ is plotted as a green curve. Although the spectral shapes are different, their overall magnitudes are comparable, as seen by the red curve both dipping below and rising above the green curve. We did not have as direct, careful measurements of the LED bias spectra for the other measurements shown in Figure S4(a). Instead, the LED intensity was estimated using the above measurement for set #2 front (red curve) as a reference, and denoting it $S_0(\lambda)$, and with knowledge that changing the LED current or sample distance preserves the shape of the spectrum, one can write $S_{LED}(\lambda) = fS_0(\lambda)$, for constant factor f. From knowledge of the EQE and bias photocurrent (a direct result of the LED illumination), and Equation S2 below, f was solved for each EQE measurement, and the rest of the incident power spectra so estimated, which are plotted in Figure S4(b). It is seen that the original EQE measurements (set #1) were performed under greater than standard 1-Sun conditions. Nevertheless, it is apparent from Figure S4(a) that the EQE itself was not sensitive to the light bias intensity in this operational range.

Figure S4(c) shows the current-potential curve measured for light bias conditions corresponding to the set #2 front EQE measurement. The photocurrent I_{ph} of the sample is related to $S_{LED}(\lambda)$ and EQE(λ) by the following integral over the relevant wavelength range:

$$I_{ph} = k \int \lambda S_{LED}(\lambda) EQE(\lambda) d\lambda \tag{S2}$$

where the factors of constant k and wavelength λ are to convert the units to result in units of electrical current. As described above, $S_{LED}(\lambda)$ was carefully measured at the sample position at the time of measurement set #2, with the LED current set to 1000 mA as in the front illumination EQE measurement. Under this light bias condition, the EQE of the sample was measured at a number of potentials. The corresponding integrals (Equation S2) for each potential are plotted in Figure S4(c) along with the measured cyclic-voltammetry curve. As shown in the figure, the integrations are reasonably close to the measured current. The log scale in the inset of Figure S4(c) reveals further agreement even when the current is near-zero (~ 2)

µA at 1.4 V_{RHE}). Likely sources of error in EQE would include alignment of the spot of the probe beam on sample and/or on the normalization photodetector. This would only result in a constant magnitude factor applied to the whole spectrum, while maintaining the spectral shape. We note that the absolute accuracy of the magnitude is not crucial for the analysis presented in the article, with the shape of the spectrum being most important. The shapes of the EQE spectra as the potential is changed, corresponding to the points in Figure S4(c), are compared in Figure S4(d). They are plotted on the same scale by multiplying by a scaling factor as indicated in the legend. This factor indicates the reduction of the EQE magnitude with respect to its value at 1.8 V_{RHE} . The shapes of the 1.6 and 1.5 V_{RHE} spectra (black line and red dots, respectively) exactly overlap even with a factor of \sim 3 between the EQE magnitudes. The 1.4 V_{RHE} (blue) spectrum, a factor of ~60 lower magnitude, is also reasonably close, with the main distortion being that the 400 nm peak is increased by a few percent relative to the rest of the spectrum. At 1.3 V_{RHE} (cyan), the EQE reduces by a factor of 1700, down to the ~0.05% level at the peak, which pushes the limits of the instrument as seen by the noise. Nevertheless, the basic spectral shape is well preserved. Interestingly, the 400 nm peak again appears to increase on average (albeit with large scatter), suggesting a trend with potential. Aside from this possible peak increase at lower potentials, these results demonstrate that for the most part, potential has little effect on the EQE shape in our measurements.

Intensity dependence of time-resolved microwave conductivity (TRMC) measurements for hematite

This section describes the intensity dependence of the TRMC signal for hematite films. As observed in Figure S5a, the TRMC signal increases with decreasing absorbed photon fluence as denoted by the photoconductivity vs absorbed photon fluence curves (filled colored symbols) measured at various wavelengths. While we were able to obtain good signal to noise ratio at low photon fluence (below 10^{13} photons per pulse per cm²) at wavelengths below 400 nm, measurements made at high wavelengths at similar photon fluence did not yield a measurable signal due to the lower photogeneration yield observed in hematite at higher wavelengths. As a result, we chose an absorbed photon fluence ((6-8)×10¹³ photons/cm²/pulse) which would allow us to measure over as wide of a range in the visible spectrum as possible. The measurements shown in Figure 3 in the article correspond to the region where the absorbed photon fluence (open grey symbols) is relatively constant (between 400 – 550 nm) in Figure S5b.



Figure S5. (a) $\phi(\lambda) \sum \mu$ vs absorbed photon fluence for various wavelengths. (b) The absorbed photon fluence vs the wavelength for the measurements in Figure 3 of the article.

Fitting of time-resolved microwave conductivity (TRMC) transients

The TRMC transients were fit to a bi-exponentially decaying function with the form

$$f(t) = a \cdot \exp\left(\frac{-t}{\tau_1}\right) + b \cdot \exp\left(\frac{-t}{\tau_2}\right) + C. 18 \text{ curves were fit at excitation wavelengths from 410}$$

to 580 nm in 10 nm increments. The fitting yielded $\tau_1 = 30 \pm 3$ ns and $\tau_2 = 400 \pm 100$ ns. Four curves are shown below in Fig S6 as examples of the fits. The *a/b* ratio was typically 3.5.



Figure S6. Biexponential fitting of TRMC transients at various excitation wavelengths.

Consideration of Other Proposed Transient Processes – Thermal Relaxation and Polarons

In this Supplementary section we consider the possible impact of other proposed transient processes during photoexcitation, and whether they may affect our TRMC interpretation and photogeneration yield calculations. It has recently been suggested that the signal decay observed in transient absorption spectroscopy above 100 ps for hematite is directly related to thermal effects, namely heating and cooling of the lattice after carrier recombination.⁵ However, in the following we reason, from the similarity between TRMC and $\xi(\lambda)$ spectra, that the TRMC signal is not a measurement of heat dissipation as was proposed in Ref. 6. Based on our present results, if the TRMC signal would have originated from heating, then the heating would be necessarily proportional to the photocurrent, because of the agreement between the spectral profiles of TRMC and $\xi(\lambda)$, as shown in Figure 3 of the article. However, this explanation would completely neglect any heating effect from non-contributing absorption $(1-\xi(\lambda))$, which would only be valid if such excitations (e.g. ligand field) only recombine radiatively and thus not contribute to the heating. The latter possibility seems unlikely because Figure 3 suggests that a large component of the absorption is non-contributing, yet it is well known that hematite does not exhibit strong photoluminescence.⁷ The close agreement between $\xi(\lambda)$ extracted from d.c. measurements of the photocurrent and $\phi \sum \mu$ extracted from microwave photoconductivity measurements is, on the other hand, more consistent with the picture that TRMC is probing the polaronic charge carriers that contribute to the photocurrent.

The formation of polarons following photoexcitation was concluded to occur on a timescale of a few ps from ultrafast THz photoconductivity,⁶ XUV spectroscopy,⁸ and most recently from "pump-push" photocurrent measurements.⁹ The lifetime of these polaronic charge carriers has been suggested to be on the order of ns and longer,⁹ consistent with the present results. This scenario of ultra-short lifetime, but mobile carriers that condense into less mobile polarons, would not nominally be expected to affect the calculation nor the meaning of $\xi(\lambda)$. As both of the pre-condensed and post-condensed excitations are mobile (varying only in degree), they would both count as "mobile charges", and the ultrashort lifetime before polaron condensation means that they would condense well before reaching the surface and contributing to the EQE measurements, so all of the original assumptions, particularly constant p(x) for each excited charge, would still effectively hold.

Transmission Electron Microscopy

The low magnification cross sectional TEM micrograph shown in Figure S7a displays the layered glass/ITO/Sn-doped hematite photoanode structure. Figure S7b shows the sharp interface between the ITO/hematite layers and the crystallinity of the layers. High angle annular dark field (HAADF) micrographs and energy dispersive X-ray spectroscopy (EDS) maps were acquired in scanning transmission electron microscopy (STEM) mode. Figure S8a shows the HAADF micrograph of the hematite photoelectrode and Figure S8b shows the accompanying EDS maps. From the figures, the conformal coverage and sharp interfaces between the layers are evident. The hematite film thickness is 7 nm.





Figure S7. (a) Low and (b) high magnification TEM cross-sectional micrographs of the ultrathin glass/ITO/hematite photoanode.



Figure S8. STEM-HAADF micrographs and EDS elemental maps (In, Sn, Fe, O) of the ultrathin hematite photoanode.



Figure S9. Absorption coefficient spectra of the 7 nm thick hematite film used in the ultrathin film photogeneration yield analysis and a 150 nm thick hematite film used in the TRMC analysis. The latter was estimated from the spectrophotometry data, assuming Beer-Lambert law intensity decay within the film and all the reflection coming from the front interface.

Extension of photogeneration yield analysis to TiO₂ and BiVO₄ photoanodes

The same general methods and analysis as used for hematite, described in the article, were applied to TiO₂ and BiVO₄ ultrathin film photoanodes. We did not use light bias for the presented EQE measurements of these films as we observed no difference between measurements with and without light bias. We fabricated the ultrathin (11 nm thick) films of Nb-doped TiO₂ and BiVO₄ by pulsed laser deposition. Because TiO₂ has a wide bandgap comparable to that of ITO, a higher-bandgap current collector was required for the TiO₂, such as Nb-doped SnO₂ (NTO), which is highly transparent in the region where TiO₂ absorbs as demonstrated in Figure S10a. Accordingly, the Nb-doped TiO₂ film was deposited on an NTO current collector, the latter deposited on sapphire (0001). The undoped BiVO₄ films were deposited on the usual ITO layers, deposited on eagle glass. A thicker 100 nm film was deposited on a fused silica substrate for TRMC measurements.

The TiO₂ sample was measured in front illumination configuration. Figure S10(a) shows the measured reflectance, transmittance and absorptance of the TiO₂ sample, along with the values predicted from the ellipsometry-derived model. The fit is generally excellent across the measured spectrum. Figure S10(b) compares the absorption in the TiO₂ layer to the EQE, measured at zero light bias and at a potential of 1.8 V_{RHE}. Both spectra plateau at around 320 nm, with the EQE falling off to approximately zero at around 400 nm. The extracted photogeneration yield is plotted in Figure S10(c). This implies that the non-zero absorptance

at wavelengths greater than 400 nm in the spectrophotometer measurement Figure S10(a), in any event, does not contribute to mobile charge generation. As expected from the similar shapes of EQE and absorption in Figure S10(b), the photogeneration yield, $\bar{p}\xi(\lambda)$, is quite flat at high energy.



Figure S10. Ultrathin (11 nm) film TiO₂ photoanode measurements (front illumination): (a) Measured (solid line) and calculated (dashed line) transmittance (T, red), reflectance (R, blue) and absorptance (F_A, green) spectra in front illumination in air. The black dashed line corresponds to absorptance only in the TiO₂ layer (A_{TiO_2}). (b) The calculated absorptance spectra in the TiO₂ layer in electrolyte (dashed lines) and measured EQE spectra (solid lines) at 1.8 V_{RHE}. (c) The extracted $\bar{p}\xi(\lambda)$ spectrum.

For the BiVO₄ photoanode, the optical model and spectrophotometry measurements, for both front and back illumination, were in good agreement as plotted in Figures S11(a) and S11(b). EQE was measured in a buffer solution with 0.21 M KH₂PO₄ and 0.29 M K₂HPO₄, with 0.05 M Na₂SO₃ hole scavenger, for a pH of 7. To be consistent with the current literature, no light bias was used for the measurement, which was done at a potential of 1.2 V_{RHE}. Front and back illumination measurements are shown in Figures S11(c) and S11(d) respectively, overlayed with the respective absorptances. The shapes of the EQE and absorptance spectra are quite

similar for both front and back illumination. A comparison of the photogeneration yield profiles calculated for front and back illumination is plotted in Figure S11e. The spectra show good agreement across the absorption spectrum of BiVO₄. Furthermore, both spectra reach values of ~100% at wavelength of 370 nm, which suggests there is little issue of charge transport within the film, meaning that \bar{p} is close to 1, and the observed losses may stem from non-unity photogeneration of charge carriers. Further supporting this assertion is a comparison to the internal quantum efficiency (IQE, also known as absorbed photon to current efficiency, APCE) of thick (~200 nm) high performing undoped polycrystalline BiVO₄ photoanodes measured in back illumination (Figure S11f), which are nearly identical to the photogeneration yield spectra.^{10,11} Interestingly, in Ref. 10 the front illumination IQE was significantly lower than the back illumination $\bar{p}\xi(\lambda)$ spectra suggests there is no limitation related to electron transport in the ultrathin film studied in this work and that photogeneration of charge carriers is potentially responsible for the observed behavior.



Figure S11. BiVO₄ ultrathin (11 nm) film measurements: Measured (solid line) and calculated (dashed line) transmittance (T, red), reflectance (R, blue) and absorptance (F_A, green) spectra in (a) front illumination and (b) back illumination in air. The black dotted line is the calculated absorptance in the BiVO₄ layer only (A_{BiVO₄}). (c) and (d): The calculated absorptance spectra in the BiVO₄ layer in electrolyte (dashed lines) and measured EQE spectra (solid lines). (e) The calculated $\bar{p}\xi(\lambda)$ product for front (black) and back (blue) illumination. (f) Comparison of photogeneration yield spectra compared with back illumination IQE (APCE) of high performing undoped BiVO₄ reported in Refs¹⁰ and¹¹.

We also performed TRMC measurements on the thicker 100 nm BiVO₄ sample. As shown in Figure S12a, the measured TRMC signals ($\Delta \sigma_{max}/I_0$), un-normalized by absorptance, generally tracks the absorptance spectrum, but we note a distinct peak-like feature around 370 nm.



Figure S12. (a) $\Delta \sigma_{\text{max}} / I_0$ (blue, left y-axis) and F_A (orange, right y-axis) spectra extracted from TRMC measurements of BiVO₄ films. (b) Comparison of $\bar{p}\xi(\lambda)$ product for an ultrathin (11 nm) BiVO₄ film photoanode and $\phi(\lambda) \Sigma \mu$ extracted from TRMC measurements of a thick BiVO₄ film deposited on fused silica. (c) Photoconductivity vs absorbed photon fluence for various wavelengths. (d) The absorbed photon fluence vs the wavelength for the measurements in Figure S12b.

Figure S12b compares the calculated photogeneration yield and TRMC-derived $\phi(\lambda) \sum \mu$ spectra. The low-wavelength region suggests agreement between the two techniques, as a main peak at ~370 nm is observed for both of them. However, variations in the absorbed photon fluence between measurements makes a quantitative comparison difficult, especially given the strong light intensity dependence on the TRMC signal for BiVO₄ as shown in Figure S12c. At higher wavelengths the two measurements deviate, with the TRMC spectrum going higher. However, both show a drop at around 475 nm, which occurs at a slightly higher wavelength

for the TRMC measurement. It can therefore be viewed that the TRMC and $\xi(\lambda)$ spectra in BiVO₄ share basically the same features, but the high-wavelength region has more spectral weight in the case of TRMC. We speculate that this difference in relative spectral weights to the high and low wavelength regions may originate from a non-linear intensity-related effect in BiVO₄,¹² since the TRMC measurement uses much higher light intensities than does the EQE measurement.

Effect of photogeneration yield on photoelectrode performance under solar illumination

In this Supplementary section we present a plot of extractable photocurrent for the studied materials for a hypothetical fully absorbing film with p(x) = 1 everywhere, as described in the article. Preliminary to this plot, we recast Figure 4 in the article in Figure S13 below, which shows the absorption spectra of the materials studied divided into contributing and non-contributing components, like Figure 4 in the article, except that in this figure the insets show the percentages of non-contributing absorption, $1 - \xi_{max}(\lambda)$, where $\xi_{max}(\lambda)$ is the upper bound of the photogeneration yield, estimated as described in the article. Referring to the insets of Figure S13(a) and (b), we see that hematite has a fairly wide wavelength range (>100 nm) above ~500 nm where the percentage loss is maintained in the ~30%-50% range. By contrast, for both TiO₂ and BiVO₄ (Figure S13(c) and (d), respectively), the percent loss absorption is very low over the regions of high absorption and sharply increases to 100% over a ~50 nm transition range below the absorption edge, indicating a relatively sharp transition between contributing mobile carrier generation and a non-contributing absorption tail.



Figure S13. Contributing absorption spectra and non-contributing percentage. Absorption coefficient (α , black curve) and average effective absorption coefficient ($\alpha \cdot \xi$, orange curve) of (a) 7 nm thick hematite film, (b) estimate for 150 nm thick hematite film (described in the article), (c) 11 nm thick TiO₂ film, and (d) 10 nm thick BiVO₄ film. For the ultrathin film cases in panels (a), (c), and (d), the effective absorption coefficient values were estimated from $\bar{p}\xi(\lambda)$ spectra extracted from EQE measurements by setting lower and upper limits, where the lower limit (dashed line) corresponds to $\bar{p} = 1$ and the upper limit (dashed line) corresponds to $\xi_{max}(\lambda) = 1$. The insets of (a)-(d) show the percentage of the non-contributing absorption, 100% $[1 - \xi_{max}(\lambda)]$, based on the upper limit estimate for $\xi(\lambda)$.

Figure S14a compares, for the different materials, the solar photon flux absorbed into contributing excitations by multiplying the standard (AM1.5G) solar photon flux spectrum by the best- and worst-case $\bar{p}\xi(\lambda)$ spectra for each material, assuming a fully absorbing layer (A=1 for all wavelengths below the absorption edge) and that all the mobile photogenerated charge carriers could be fully extracted with a collection efficiency of 100% (p(x)=1). On one hand, high $\xi(\lambda)$ of both TiO₂ and BiVO₄ allow them to make almost full use of the solar spectrum in

their respective wavelength ranges, but on the other hand the total utilized flux is limited by their relatively sharp cut-offs of contributing mobile absorption. By comparison, inspection of Figure S14a shows that the $\xi(\lambda)$ effect in hematite causes a relatively low percentage of solar flux density to go into contributing carrier photogeneration (especially for $\xi(\lambda) < \xi_{max}(\lambda)$) over a wide wavelength range, significantly limiting the maximum achievable photocurrent. Figure S14b is a plot of the contributing solar flux density for hematite from Figure S14a, integrated over the range (350 - 590nm), and converted into attainable photocurrent density. The best and worst scenarios for $\xi(\lambda)$ are compared with the maximal theoretical efficiency based on absorption above the band gap. This results in a maximal attainable photocurrent density (assuming a carrier collection efficiency of 100%) of 3.4 to 8.5 mA/cm², significantly lower than that based on absorbed value of 12.3 mA/cm² in this wavelength range.



Figure S14. (a) Amount of solar photon flux (black) absorbed into contributing excitations by the BiVO₄ (green), TiO₂ (blue), and α -Fe₂O₃ (red), respectively, calculated based on a fully absorbing film, as described in the article. The solid lines correspond to the median estimation, while the dotted lines correspond to the upper and lower bounds, which differ considerably for hematite. (b) Total photocurrent density attainable by hematite from the solar spectrum between 350 and 590 nm, based on the best- and worst-case $\bar{p}\xi(\lambda)$ spectra.

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