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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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Light absorption in strongly correlated electron materials can excite electrons and holes into a variety of different states. Some of these excitations yield mobile charge carriers, whereas others result in localized states that cannot contribute to photocurrent. The photogeneration yield spectrum, $\xi(\lambda)$, represents the wavelength-dependent ratio between the contributing absorption that ultimately generates mobile charge carriers and the overall absorption. Despite being a vital material property, it is not trivial to characterize. Here, we present an empirical method to extract $\xi(\lambda)$ through optical and external quantum efficiency measurements of ultrathin films. We applied this method to haematite photoanodes for water photo-oxidation, and observed that it is self-consistent for different illumination conditions and applied potentials. We found agreement between the extracted $\xi(\lambda)$ spectrum and the photoconductivity spectrum measured by time-resolved microwave conductivity. These measurements revealed that mobile charge carrier generation increases with increasing energy across haematite's absorption spectrum. Low-energy non-contributing absorption fundamentally limits the photoconversion efficiency of haematite photo-anodes and provides an upper limit to the achievable photocurrent that is substantially lower than that predicted based solely on absorption above the bandgap. We extended our analysis to TiO₂ and BiVO₄ photoanodes, demonstrating the broader utility of the method for determining $\xi(\lambda)$.

t the heart of any semiconductor photoabsorber material in photovoltaic and photoelectrochemical cells for solar energy conversion is the ability to absorb light and thereby generate excess mobile charge carriers (electrons and holes) that give rise to photocurrent and photovoltage¹. Many photoabsorber materials have intricate and complex electronic and optical properties, to the effect that light can excite electrons and holes into a variety of different states. Although some of these optically excited states are or can eventually become mobile charge carriers, others are localized and cannot contribute to photocurrent. These non-contributing absorption processes include ligand field $(d \rightarrow d)$ excitations that can be optically allowed by distortions from inversion symmetry and many-body effects^{2,3}. Likewise, organic photovoltaic materials also have different types of photoexcitations and excitons, which have a direct impact on the photocurrent^{4,5}. The various types of optical excitations, contributing and non-contributing ones, can overlap in wavelength across the material's absorption spectrum. The wavelength-dependent ratio between the contributing and overall absorption defines the photogeneration yield spectrum, $\xi(\lambda)$, equivalent to the probability that an absorbed photon of wavelength λ will ultimately generate a mobile charge carrier. This quantity is therefore of core importance for the development of photovoltaic and photoelectrochemical devices. However, $\xi(\lambda)$ can be difficult to properly characterize, because most of the pertinent measurements can only detect the photocurrent action spectrum, $J_{\rm ph}(\lambda)$, which comprises different optical and electronic factors. An intermingling

of the inherent material properties (for example, absorption processes and cross-sections, electronic transport and recombination mechanisms in bulk and through surface, optical constants), and the more macroscopic-level, adjustable properties (for example, lengths and interfaces) of the device tested, are all factors that combine to produce $J_{\rm ph}(\lambda)$ for the particular device. It is therefore desirable, as a basic measure, to characterize the system by only a few basic parameters, including $\xi(\lambda)$, that have straightforward physical definitions.

Here, we present a method for extracting $\xi(\lambda)$ empirically, without any a priori assumptions about its shape. The derivation begins from a spatial collection efficiency model^{6,7}, but using ultrathin films to remove all the spatial effects, thereby greatly simplifying the computation and avoiding a priori assumptions. As a case study, we first applied this method to study haematite (α -Fe₂O₃) photoanodes for water photo-oxidation in photoelectrochemical (PEC) cells for solar water splitting⁸. We then compared the results with those obtained from photoconductivity measurements using an entirely different, non-contact technique, namely time-resolved microwave photoconductivity (TRMC), which should, in principle, provide an action spectrum that is also proportional to $\xi(\lambda)$ if the charge carrier mobility is wavelength-independent9. Consistent with this prediction, the shapes of the extracted $\xi(\lambda)$ and TRMC action spectra were found to be similar. The consistency between these two diverse techniques, one an entirely direct-current method in a PEC cell under applied bias, the other a totally non-contact method at

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microwave frequencies, demonstrates that both methods probe the same fundamental material property, and affirms that, in addition to being a guide for accurate device characterization, modelling and design, they provide invaluable insight into the material's inherent light absorption processes.

A standard measure of photovoltaic or PEC device performance is the photocurrent action spectrum $J_{\rm ph}(\lambda)$, normalized by the incident light spectrum, known as the external quantum efficiency (EQE, synonymous with incident photon to electron conversion efficiency, IPCE)^{10,11}. For haematite, it has long been noticed that its EQE falls off with increasing wavelength, at a rate beyond what would be expected from the decreasing optical absorption¹². This observed discrepancy is common to all haematite photoanodes, even when considering spatial effects of where the light is absorbed in the sample¹³. Different interpretations have been hypothesized to describe this phenomenon, and are still under debate. The first was suggested by Kennedy and Frese, who attributed the wavelength-dependent photocurrent action spectrum to the existence of multiple absorption bands, only one of which generates mobile charge carriers that contribute to the photocurrent, thereby resulting in a less than unity value of $\xi(\lambda)$ at different wavelengths¹². More recently, this notion of differentiating between the contributions of holes excited at different wavelengths was revived in a few reports^{14,15}, and a similar suggestion has been made by Hayes et al., with assignment of the absorption spectrum to a combination of overlapping ligand-to-metal charge-transfer (LMCT) and ligand field excitations³. Consistent with this general picture, Braun et al. found evidence in the X-ray absorption spectrum of oxygen for the generation of two kinds of holes in haematite under illumination¹⁶. An alternative explanation for the wavelength dependence, based on the interpretation of ultrafast extreme ultraviolet spectroscopy, has been recently suggested by Carneiro et al.¹⁷. In their model, higher-energy excitation results in photogenerated polaronic charge carriers with greater mobility and longer lifetimes. In light of these intriguing reports, there is a clear need for spectrally resolved characterization of how optical absorption mechanisms affect mobile charge carrier yield in strongly correlated electron materials such as haematite², in which the absorption of above-bandgap photons do not necessarily produce free electrons and holes as they do in covalent semiconductors such as silicon. In this study we have developed an empirical method for accurate determination of the spectral profile of $\xi(\lambda)$ for haematite as a case study, followed by TiO₂ and BiVO₄ as additional examples, and together with complementary observations from TRMC, we demonstrate here its value for understanding the nature of optical absorption mechanisms and charge carrier generation, and for re-evaluating fundamental device limits.

We derived the empirical extraction of $\xi(\lambda)$ from a one-dimensional spatial collection efficiency model, which was used to deduce the probability p(x) of a charge carrier generated at distance *x* from the surface reaching and making it across the surface at x = 0 without recombining^{6,7,18}. The model uses the measured EQE spectrum combined with measured optical properties of the device, without any a priori assumptions. The EQE spectrum can be constructed by the following integral over the photoabsorber layer thickness *d*:

$$EQE(\lambda) = \int_{0}^{d} \frac{I(\lambda, x)}{I_{0}(\lambda)} \alpha(\lambda) \xi(\lambda) p(x) \, dx$$
(1)

where $I(\lambda, x)$ is the wavelength-dependent photon flux at point x, normalized by the incident flux $I_0(\lambda)$ at the surface (x=0), and $\alpha(\lambda)$ is the optical absorption coefficient of the photoabsorber layer. In equation (1), the product $I(\lambda, x)\alpha(\lambda)\xi(\lambda)$ describes the mobile charge carrier generation, while charge transport and recombination effects are contained in p(x), which is assumed to be wavelength-independent. This assumption is supported by previous TRMC measurements in haematite that showed that the photoconductivity lifetimes do not change with excitation wavelength9. Similar conclusions have been made for other photoabsorber materials¹⁹. The analysis takes into account that the depth of optical penetration is wavelength-dependent, which has a substantial impact on the photocurrent action spectrum when the mean minority charge carrier collection length is less than the thickness of the photoabsorber layer. Experimentally, EQE(λ) is directly measured, while $I(\lambda, x)$ and $\alpha(\lambda)$ can be extracted from spectroscopic ellipsometry^{20,21}. The remaining unknowns, $\xi(\lambda)$ and p(x), are typically solved by numerical procedures7. For conventional photoabsorber materials such as silicon, where $\xi(\lambda) = 1$ throughout the absorption spectrum, this method has been applied successfully to obtain p(x)(ref. 6), and most prior analyses have indeed neglected $\xi(\lambda)^{6,22,23}$. A similar approach was also adopted recently for complex metal oxide photoabsorbers such as copper vanadate²⁴ and for colloidal quantum dot solar cells²⁵. For non-trivial, unknown $\xi(\lambda)$, as is the case for strongly correlated electron materials such as haematite², it can be a daunting task to solve equation (1), requiring several numerical steps and a priori assumptions7. This task falls into the category of ill-posed inverse problems, which may have multiple solutions, of which only one is the correct physical solution²³. However, if the layer thickness d is small relative to the length scale of the spatial variation in both $I(\lambda, x)$ and p(x), then all of the spatial variations can be replaced by their respective spatially averaged values, $\overline{I}(\lambda)$ and \overline{p} . A detailed analysis of the error introduced by this approximation is given in the Supplementary Information. Under those conditions, equation (1) can be simplified as a product of averages and explicitly solved for $\xi(\lambda)$:

$$\xi(\lambda) \cong \lim_{d \to 0} \left\{ \frac{\mathrm{EQE}(\lambda)}{\alpha(\lambda)d} \right\} \frac{1}{\frac{\overline{I}(\lambda)}{\overline{I_0}(\lambda)}\overline{p}}$$
(2)

For highest accuracy, $\overline{I}(\lambda)$ would ideally be obtained from optical modelling, such as from spectroscopic ellipsometry or other methods appropriate to the optical stack²⁶. These methods would allow one to accurately account for effects such as multiple reflections and parasitic absorption in other layers, which could have a profound effect on the results. However, if a sufficiently accurate optical model is not available, a crude approximation would be that most of the optical losses in the limit of small $d(d \ll \alpha^{-1})$ come from interface reflection, and therefore $\lim_{d\to 0} \frac{\overline{I}(\lambda)}{I_0(\lambda)} \approx 1 - R(\lambda)$, where *R* is the reflector $I_0(\lambda)$ is the reflector $I_0(\lambda)$. the reflectance. With this latter substitution, equation (2) resembles the classical equation for internal quantum efficiency (IQE), divided by a factor \bar{p} , which also becomes evident by equating $\alpha d(I/I_0)$ in the denominator of equation (2) with the absorptance. We emphasize that only absorption in the photoabsorber layer should be considered. Improper accounting for absorption in each layer in the optical stack (comprising a substrate, current collector, photoabsorber and possibly other layers), whereby light absorbed in non-contributing layers is erroneously included in the calculation, can adversely affect the analysis accuracy. Additionally, if the thickness *d* of the photoabsorber layer becomes comparable to the length scale of variations of p(x) and $I(\lambda, x)$, the resultant $\xi(\lambda)$ spectrum from the 'IQE-like' approximation (equation (2)) will be distorted by spatial p(x) and I(x) effects. Previous works emphasized the importance of correct optical modelling using the transfer matrix method^{18,20,26}, however, $\xi(\lambda)$ itself was not accounted for, which we demonstrate below to be an important effect in the case of haematite. Finally, it is important that the electrolyte solution is taken into account in the optical model, as it can substantially affect the reflection and absorptance in the photoabsorber during the EQE measurement.

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To ensure the validity of the small d condition for equation (2) in our case study, we simulated different thicknesses to see how it affects the error in the approximation, and the results are presented in the Supplementary Information and Supplementary Figs. 2 and 3. The simulations show that haematite films with a thickness of less than 10 nm would be required to keep the error down to a few per cent. Therefore, a 7-nm-thick film of Sn-doped haematite was deposited using pulsed laser deposition (PLD) on an indium tin oxide (ITO)-coated glass substrate. Spectroscopic ellipsometry was used to extract the optical constants of the ITO and haematite layers in the stack to create an accurate optical model for light absorption in the sample. The thicknesses of the films extracted from cross-section transmission electron microscopy (TEM) were used to guide the optical modelling. It has been reported that for film thicknesses under ~20 nm, the optical spectra of haematite thin films may be affected by structural or quantum size effects^{27,28}. Consistent with these previous observations, the absorption coefficient of the 7-nm-thick haematite film shows a blueshift of the main near-ultraviolet peak, as well as an apparent suppression of the feature at ~550 nm, relative to that of a 150-nm-thick haematite film (Supplementary Fig. 9). To validate the extracted optical constants, transmission and reflection measurements were performed with a spectrophotometer, and the results compared with those of the optical simulations performed using the transfer matrix method with the model's optical parameters. Figure 1a shows excellent agreement between the model simulations and the transmittance (T) and reflectance (R) measurements over a wide wavelength range. The total absorptance, that is, the total fraction of photons absorbed in the sample out of the incident photon flux, given by $F_A = 1 - R - T$, is also plotted in Fig. 1a, along with the absorptance in only the haematite film, $A_{\text{haematite}} = \alpha d(\bar{I}/I_0)$. The difference between the absorptance of the full stack (F_A in Fig. 1a) and of the haematite layer highlights the importance of accounting for parasitic absorption in the ITO current collector and glass substrate in the optical model, and it follows that spectrophotometer measurements alone may not be sufficient for accurate analysis. A similar optical analysis was performed for back illumination and the results are presented in Supplementary Fig. 1.

The photoelectrochemical EQE measurements were performed with a custom system that can measure $EQE(\lambda)$ with low noise under a light bias from a white-light-emitting diode (LED) source at approximately 1 Sun intensity (described in detail in the Methods and Supplementary Information). Figure 1b shows the EQE spectra for the cases of the wavelength-varying probe light incident on the front or back side of the film, while maintaining the same white-light bias conditions on the front of the sample. We note that the monochromatic probe light is typically 100 times weaker than the LED bias, so sample conditions such as surface band-bending are maintained solely by the potential and LED bias irrespective of whether the probe light is applied to the front or back of the sample. Also shown in Fig. 1b are the respective absorptance spectra of the haematite layer calculated with the inclusion of the electrolyte layer, which has a different index of refraction from air, in the optical model. Substantial differences are apparent between front and back illumination for both the haematite layer absorptance and EQE spectra. Applying both sets of data to equation (2) resulted in the respective spectra of $\bar{p}\xi(\lambda)$, which are presented in Fig. 1c. We emphasize that these come directly from the EQE measurements and optical model calculations (supported by spectroscopic ellipsometry and spectrophotometry measurements), without any offsets or scaling. Because the applied potential and light bias conditions on the sample are the same for both cases, the average charge carrier collection probability \bar{p} should be unchanged.

Because the value of \bar{p} is unknown, we cannot extract the absolute magnitude of $\xi(\lambda)$, but we can extract its spectral profile. The consistency of the $\bar{p}\xi(\lambda)$ spectra resulting from the rather diverse



Fig. 1 | Extraction of the photogeneration yield spectrum from optical and photoelectrochemical EQE measurements of a 7-nm-thick haematite film. a, Measured (solid line) and calculated (dashed line) transmittance (*T*), reflectance (*R*) and absorptance (*F*_A) spectra in front illumination in air. The calculated absorptance in the haematite layer only ($A_{haematite}$) is also shown. **b**, The calculated haematite absorptance spectra in water and EQE spectra measured at 1.6 V_{RHE} in front and back illumination (FI and BI, respectively). **c**, The extracted $\bar{p}\xi(\lambda)$ spectra for front (black) and back (blue) illumination.

datasets of front and back illumination validates our approach, and verifies that the 7-nm haematite film meets the requirement for the applicability of equation (2). The differences between these two derived spectra can be considered as a gauge of the error in the analysis. We note some similarity of the $\xi(\lambda)$ spectra in Fig. 1c with the IQE spectra measured in haematite thin films²⁹ and nanostructures³⁰. Nanostructured porous layers in which lateral charge collection dominates8 could potentially have a relaxed thickness requirement for estimating $\xi(\lambda)$, but require increased complexity of optical modelling as compared with dense ultrathin films. Changing the applied potential had very little effect on the EQE shape, as described in the Supplementary Information. Supplementary Fig. 4d shows only a small change in the peak height at ~400 nm, even as the value of EQE decreases by three orders of magnitude. It follows that $\xi(\lambda)$ is likewise independent of the applied potential, unless the absorptance changes its spectral shape but EQE does not. Previous PEC spectrometric studies of haematite photoanodes showed that the steady-state absorptance at a wavelength of ~580 nm changes by only a fraction of a per cent when applying a potential of 1.6 V versus the reversible hydrogen electrode (RHE) scale (V_{RHE}), which would have a negligible effect on $\xi(\lambda)^{31}$. This implies that the applied potential only affects p(x), presumably through p(0) at x = 0, which is the potential-dependent charge-transfer efficiency at the surface, and it is independent of the photoexcitation wavelength. That the EQE spectral shape does not change by changing p(x) gives some credence to the premise that p(x) is independent of wavelength for the haematite film. This is consistent with the wavelength-independent lifetimes of photogenerated charge carriers previously measured by TRMC and presented below9. The wavelength independence of photogenerated hole behaviour at the surface was also confirmed by transient photocurrent versus surface charge measurements¹⁴.

Although accurate extraction of $\xi(\lambda)$ (multiplied by a factor of \bar{p}) has been demonstrated above for an ultrathin haematite film, one might ask whether this spectrum is indicative of $\xi(\lambda)$ for a thicker haematite film, given the possibility of quantum confinement effects in ultrathin films^{27,28}. It would therefore be useful to compare this approach with another measurement technique that nominally measures a quantity similar to $\xi(\lambda)$, but that does not require ultrathin films in which quantum confinement could be prevalent. One such method is TRMC, a contactless pump-probe technique in which the sample is placed in a microwave cavity and excited by a nanosecond laser pulse^{9,32}. The resulting transient photoconductivity, $\Delta\sigma(t)$, in the sample is probed by monitoring light-induced changes in the cavity's reflected microwave power, $\frac{\Delta P}{P}(t)$, described by the following relation:

$$\frac{\Delta P}{P}(t) = -K\Delta\sigma(t) \tag{3}$$

where *K* is a sensitivity factor that depends on resonance characteristics and the properties of the cavity and sample³³. The ratio between the amount of mobile charge carriers probed by the microwave and the absorbed photon fluence is defined as the quantum yield, ϕ . We note that ϕ is equivalent, in principle, to the previously defined photogeneration yield. Supporting this notion, previous studies on organic semiconductor materials have suggested a link between the IQE measured in photovoltaic devices and the photogenerated charge carrier yield probed by TRMC^{34,35}. The product of ϕ and the sum of the electron and hole mobilities, $\sum \mu = \mu_e + \mu_h$ (or $\phi \sum \mu$ for brevity), can be related to the change in peak photoconductivity prior to recombination, $\Delta \sigma_{max}$, extracted from the TRMC measurement by:³²

$$\phi \sum \mu = \frac{\Delta \sigma_{\max}(\lambda)}{e I_0(\lambda) F_A(\lambda)/d} \tag{4}$$

where $I_0(\lambda)$ is the number of incident photons per cm² per pulse (we note I_0 in equation (4) refers to fluence per pulse, different from I_0

defined in equations (1) and (2) as flux per second) and *e* is the elementary charge. As TRMC measurements are performed in air on transparent substrates (sapphire in our case) without parasitically absorbing current collectors, we can approximate that the total absorptance, F_A , is equal to the absorptance in the haematite film, $A_{\text{haematite}}$. In equation (4), the product of the quantum yield and mobility sum is presented as the peak conductivity change normalized by the product of the elementary charge and average volume density of absorbed photons per pulse, $eI_0(\lambda)F_A(\lambda)/d$. Owing to experimental uncertainty in the quantification of *K*, which is independent of excitation wavelength, and because we are primarily interested in spectral or temporal shapes, we present our results in arbitrary units, noting that $\phi \sum \mu$ is proportional to $\frac{\Delta \sigma_{max}(\lambda)}{I_0(\lambda)F_A(\lambda)}$.

TRMC measurements were performed on an heteroepitaxial 150-nm-thick (0001)-oriented Sn-doped haematite film deposited on c-plane sapphire. Measurements were carried out at various wavelengths across haematite's absorption spectrum (from 405 to 590 nm) in increments of 5 nm. Given the intensity dependence of the TRMC signal, as discussed in the Supplementary Information and shown in Supplementary Fig. 5, neutral density filters were selected to keep the absorbed photon fluence as constant as possible (between 6×10^{13} and 8×10^{13} photons per pulse per cm²) over the wavelength range measured. The transient photoconductivity response for selected wavelengths is plotted in Fig. 2a. As can be seen, $\Delta \sigma_{\text{max}}/(F_{\text{A}}I_0)$, proportional to $\phi \sum \mu$, varies with excitation wavelength, suggesting that either ϕ or $\sum \mu$ (or both) vary with wavelength. Because the TRMC measurement cannot directly distinguish the variables within the $\phi \sum \mu$ product, it is non-trivial to determine which of either the quantum yield or effective mobility is responsible for the wavelength dependence. However, a closer look at the charge carrier decay dynamics provides a compelling indication. Figure 2b shows that when the transient photoconductivity is normalized by its peak value, the decay dynamics are identical for different excitation wavelengths on the nanosecond timescale of our TRMC experiments. The transients were fitted to a biexponentially decaying function, as described in the Supplementary Information, and the fitted time constant of the fast decay was determined to be 30 ± 3 ns across the entire wavelength range. This indicates that the TRMC measurements probe mobile charge carriers with the same dynamics throughout the entire wavelength range, implying that the wavelength dependence of the TRMC response likely originates from the variation in the quantum yield, ϕ , rather than a change in the mobilities, $\Sigma \mu$ (ref. ¹⁹). Various processes have recently been proposed to occur over fast timescales during photoexcitation, such as self-heating³ or the formation of polarons¹⁷, which are potentially relevant and should not be overlooked in relation to the present analysis. We briefly review these processes in the Supplementary Information and present arguments that heat dissipation is not responsible for the TRMC signal and can instead be attributed to polaronic charge transport. The formation of polarons following photoexcitation was concluded to occur on a timescale of a few picoseconds from ultrafast terahertz photoconductivity9, ultrafast extreme ultraviolet spectroscopy¹⁷ and most recently 'pump-push' photocurrent measurements³⁶. It has been suggested that the lifetime of these polaronic charge carriers is in the order of nanoseconds and longer³⁶, consistent with the present results.

If the $\phi \sum \mu$ product were independent of wavelength, as one would expect in covalent semiconductors such as silicon, then $\Delta \sigma_{max}/I_0$ would be proportional to the absorption spectrum, F_A . However, as shown in Fig. 2c, $\Delta \sigma_{max}/I_0$ plotted across the wavelength spectrum deviates from F_A . If μ remains constant and ϕ varies with wavelength, then $\phi(\lambda) \sum \mu$ should, in principle, be similar to the previously calculated $\bar{p}\xi(\lambda)$ spectrum, provided that the two films have similar photogeneration yield spectra. The $\bar{p}\xi(\lambda)$ spectrum of the 7-nm haematite film (from Fig. 1c) and the $\phi(\lambda) \sum \mu$ spectrum of the 150-nm haematite film (from Fig. 2c) are compared in Fig. 3,

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Fig. 2 | TRMC measurements of a 150-nm-thick haematite film. a, Photoconductivity transients normalized by the absorbed photon fluence measured by TRMC at different wavelengths. **b**, Photoconductivity transients normalized by the peak photoconductivity for each wavelength. **c**, Peak photoconductivity normalized by incident light intensity but not absorptance (left *y* axis), overlaid with the absorptance F_A (right *y* axis) spectra. The TRMC data are averaged over 300 measurements. The associated error bars in Fig 2c are calculated based on uncertainty in the measured incident photon fluence.

scaled by a factor so that both spectra are plotted on the same scale. Similarity between the two spectra is observed, suggesting that the two methods probe the same physical quantity, and further affirms the presented methodology to extract the shape of $\xi(\lambda)$. It also suggests that TRMC is a comparable method for probing $\xi(\lambda)$ that is not limited to ultrathin films. The variations between the spectra likely originate from the sharper features in the bulk absorption spectrum as compared with the ultrathin film (Supplementary Fig. 9).

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To elucidate the contributing and non-contributing components of absorption, we multiply $\xi(\lambda)$ by $\alpha(\lambda)$ to yield the contributing absorption coefficient for generating mobile charge carriers, $\alpha_{\rm C}(\lambda) = \xi(\lambda) \alpha(\lambda)$. Likewise, $[1 - \xi(\lambda)] \alpha(\lambda)$ represents the non-contributing absorption coefficient, which we denote as $\alpha_{\rm NC}$. Figure 4a shows the contributing and non-contributing absorption coefficients as a function of wavelength for the 7-nm-thick haematite film. Because $\xi(\lambda)$ is calculated to within a factor of \bar{p} , the absolute value of $\alpha_{\rm C}(\lambda)$ cannot be extracted with an absolute certainty. However, we can place lower and upper limits on $\alpha_{\rm c}(\lambda)$ by taking $\bar{p} = 1$ (upper dotted line in Fig. 4a) and maximal $\xi(\lambda) = 1$ (lower dotted line in Fig. 4a), respectively. We note that qualitatively, the shape of $\alpha_{\rm c}(\lambda)$ is equivalent in both cases. In the condition where $\bar{p} = 1$, this represents a 'worst-case' scenario for $\alpha_{\rm c}(\lambda)$, as it suggests that the maximum $\xi(\lambda)$ reaches approximately 40%, and most of the absorption does not contribute to the photocurrent. Even for the best-case scenario, where maximal $\xi(\lambda) = 1$ at high excitation energies, considerable losses in photogeneration are still observed throughout haematite's absorption spectrum. The real case falls somewhere between these two extremes, and hence we draw the estimated border between contributing and non-contributing absorption in Fig. 4a-d as the average between the two extreme limits. The lower limit suggests a similar ratio in contributing photogeneration (~40% at 350 nm) to what was previously reported by Kennedy and Frese $(\sim 30\%)^{12}$. However, a recent report demonstrating the EQE at 350 nm exceeding 75% suggests that the upper limit may be more realistic³⁷. Even in the best-case scenario, $\xi(\lambda)$ is reduced by approximately half towards higher wavelengths. For the 150-nm-thick haematite film, which is more representative of bulk haematite, we used the TRMC spectrum in Fig. 3c and estimated the absorption coefficient (Supplementary Fig. 9) to plot in Fig. 4b the estimated contributing and non-contributing components of its absorption. Because our TRMC data provide only the shape of the photogeneration yield spectrum, we cannot plot its lower limit as in Fig. 4a, but rather scale the average to be similar to the ultrathin-film case, indicated by the solid orange curve in Fig. 4b. The contributing and non-contributing components of the spectrum show more structure than the ultrathin film of Fig. 4a, as may be expected from the additional features observed in the absorption coefficient spectrum of the thicker film (Supplementary Fig. 9), but the same general effect on $\alpha_{\rm C}(\lambda)$ is observed. The upper limit was estimated by setting the maximum of the TRMC spectrum to correspond to $\xi(\lambda) = 1$, shown by the dotted line in Fig. 4b. From even this optimistic maximum, it is apparent from Fig. 4b that many of the absorbed photons are lost to non-contributing absorption in the haematite layer.

The salient feature in Fig. 4a is a smooth, featureless increase of the contributing component of the absorption spectrum ($\alpha_{\rm C}$) with decreasing wavelength, while any subtle wavy features in the absorption spectrum (α) are a result of non-contributing absorption $(\alpha_{\rm NC})$. To inspect the non-contributing component more closely, we subtracted the contributing component from the absorption spectrum and plotted the result in the inset of Fig. 4a, revealing a broad peak-like feature centred around 510 nm and a slight feature at around 410 nm. This behaviour is consistent with models that attribute the EQE spectrum of haematite photoelectrodes to a combination of absorption that contributes to the photocurrent and non-contributing absorption due to localized ligand field excitations^{3,12}. The monotonic decrease in $\alpha_{\rm C}$ with increasing wavelength is consistent with the assignment of Hayes et al. of a broad, high-energy LMCT band, which is responsible for mobile charge carrier generation, superimposed on non-contributing ligand field



Fig. 3 | Comparison of TRMC and photoelectrochemical EQE analysis. Comparison of the $\bar{p}\xi(\lambda)$ spectrum for an ultrathin 7-nm-thick haematite film photoanode with the $\phi(\lambda) \sum \mu$ spectrum extracted from TRMC measurements of a 150-nm-thick epitaxial haematite film deposited on sapphire. The $\phi(\lambda) \sum \mu$ spectrum was scaled to plot the data on the same *y* scale as $\bar{p}\xi(\lambda)$. The data points for the TRMC measurements in Fig 3 represent an average of 300 measurements. The solid symbols correspond to measurements taken within an absorbed fluence range of $(6-8) \times 10^{13}$ photons per cm² per pulse. The open symbols correspond to measurements are calculated based on uncertainty in the measured incident photon fluence and its effect on the measured photoconductivity. The error bars from the EQE measurements reflect the difference between the calculated $\bar{p}\xi(\lambda)$ spectra for front and back illumination.

peaks at higher wavelengths³. This mobile tail extends to at least 620 nm (2 eV), as is evident from the non-zero EQE at this wavelength (Supplementary Fig. 4). Interestingly, the non-contributing spectrum in the 150-nm-thick haematite film calculated from the TRMC spectrum, shown in the inset of Fig. 4b, has a peak at around 510 nm, similar to the ultrathin-film case, even though the absorption spectra of the two films are different. The spectra in Figure 4a,b together point to the existence of ligand field excitations centred at energies of approximately 2.4 and 3.0 eV (~510 and 410 nm, respectively). Complementary spectroscopic techniques such as resonant inelastic X-ray scattering could be used to verify the nature of the excitations at these energies. Further studies could clarify the role of charge carriers excited into the LMCT bands. Given the spectral agreement of the two techniques presented in this work and the lifetimes of the measured charge carriers, our results may be interpreted in the context of photogeneration by LMCT transitions followed by a likely decay into a longer-lived polaronic state^{17,36}.

To demonstrate the applicability of our method to probe the photogeneration yield of other photoabsorber materials, we extended the analysis to two other widely studied photoanode materials, TiO₂ and BiVO₄. TiO₂ is a transition metal oxide with a larger bandgap (~3.0 eV) than haematite $(2.0 \text{ eV})^{8,38}$, but its 3*d* states lie mostly in the conduction band and are also split by the crystal field. TiO₂ was the first reported photoanode material for PEC water splitting³⁹. BiVO₄ is a contemporary high-performance photoanode material with valence interactions between the V 3*d*, O 2*p* and Bi 6*p* states⁴⁰. Although these materials have achieved higher IQEs than haematite, distinct signatures of polaron formation were observed^{41,42}. We used the ultrathin-film approach to calculate the $\bar{p}\xi(\lambda)$ spectra of these materials as for haematite, and the

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procedures and data derived from the optical, EQE and photogeneration yield calculations are presented in the Supplementary Information and Supplementary Figs. 10-12. The resultant contributing and non-contributing components of the TiO₂ and BiVO₄ absorption spectra derived from this analysis are plotted in Fig. 4c,d, respectively, with the upper and lower limits shown as dotted lines. As expected, the extracted $\bar{p}\xi(\lambda)$ spectrum for TiO₂ (Supplementary Fig. 9) shows a relatively flat profile until falling to zero at the band edge, consistent with reports of unity photogeneration yield in TiO₂ (ref. ⁴³). Thus, the upper limit for $\alpha_{\rm C}(\lambda)$ shown in Fig. 4c is very close to $\alpha(\lambda)$. For BiVO₄, we observe a $\bar{p}\xi(\lambda)$ spectrum with a feature that reaches a maximum of 100% at ~370 nm, where there is indication for a similar maximum in the TRMC spectrum (Supplementary Fig. 12). This suggests that the charge carrier collection efficiency in this photoanode is likely close to 100% in our measurement. Interestingly, despite the much thinner film thickness and different deposition methods, the extracted photogeneration yield spectrum we obtained agrees well with the back-illumination IQE spectra of high-performance undoped BiVO₄ photoanodes reported previously^{44,45} (Supplementary Fig. 11f). This result suggests that the upper limit for undoped BiVO₄ photoelectrodes may be related to the photogeneration yield of mobile charge carriers. Charge transport and recombination effects, on the other hand, are manifested in the disparity between front- and back-illumination IQE measurements observed previously^{44,45}, but not for $\xi(\lambda)$. Further discussion is included in the Supplementary Information. Referring to Fig. 4c, the upper limit of TiO₂ confirms a unity photogeneration yield above 360 nm, and additionally, no distinct features are observed in the non-contributing absorption spectrum, suggesting the absence of localized excitations above the bandgap. The case of BiVO₄ is less clear, with the analysis suggesting regions of non-contributing absorption, notably below 350 nm (Fig. 4d). The non-contributing component, plotted in the insets of Fig. 4, shows no clear structure for TiO₂ (Fig. 4c). However, the continuing non-zero absorption for wavelengths higher than 400 nm, beyond the contributing range, could indicate a long wavelength tail of absorption into localized states. BiVO₄, in contrast, shows distinct wavy features in both of the contributing and non-contributing components of absorption (Fig. 4d). Such a result may be unexpected for a material with V 3d states that are nominally predicted to be empty, but it may be related to the ligand field excitations revealed in a recent X-ray spectroscopy study⁴⁶, which suggested some occupation of the *d* states.

For a comparison of the practical limitations that $\xi(\lambda)$ can cause under standard solar illumination conditions, we multiplied 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). In principle, this may be realized by nanostructuring⁴⁷ or resonant light trapping¹⁸. The results (Supplementary Fig. 14a) show that many photons in haematite are lost to non-contributing absorption processes, even in the best-case scenario. For a numerical comparison, we calculated the ratio of contributing photons to the total amount

of absorbed photons, equal to $\frac{\int_{\min \lambda_0}^{\lambda_{\min}} \lambda_0^{\lambda}(\lambda)\xi(\lambda)d\lambda}{\int_{\lambda_{\min}}^{\lambda_{\max}} f_{\lambda_0}^{\sup}(\lambda)d\lambda}$, within the measured

spectral range ($\lambda_{\min} < \lambda < \lambda_{\max}$). From the worst- and best-case estimates of $\xi(\lambda)$ for haematite, this provides a value of ~30–70% of the total absorbed photons between 350 and 590 nm, corresponding to a maximal photocurrent density (assuming a carrier collection efficiency of 100%) of 3.4–8.5 mA cm⁻² out of the total absorbed value of 12.3 mA cm⁻² in this wavelength range (Supplementary Fig. 14b). This result indicates that the optical loss from non-contributing absorption processes presents a



Fig. 4 | Contributing and non-contributing components of the absorption spectra. a-d, Absorption coefficient (α , black curve) and average contributing absorption coefficient (α_c , orange curve) of a 7-nm-thick haematite film (**a**), estimate for a 150-nm-thick haematite film (described in the text; **b**), an 11-nm-thick TiO₂ film (**c**) and an 11-nm-thick BiVO₄ film (**d**). For the ultrathin-film cases in panels **a**, **c** and **d**, the contributing absorption coefficient values were estimated from the $\bar{p}\xi(\lambda)$ spectra extracted from EQE measurements by setting lower and upper limits (dotted lines), where the lower limit corresponds to \bar{p} =1 and the upper limit corresponds to maximal $\xi(\lambda)$ =1. The orange and blue shading represent the contributing and non-contributing portions of the absorption spectrum, respectively, for the average estimate. The insets of **a-d** show the spectra of the non-contributing component, α_{NCr} corresponding to the upper blue-shaded regions in the main figures, along with the upper and lower limits (dotted lines).

formidable challenge to the viability of haematite as an efficient photoanode material. By contrast, TiO_2 and $BiVO_4$ photoanodes exhibit more efficient absorption than haematite, with a small optical loss due to non-contributing absorption over most of their maximum absorption range, which covers a narrower wavelength range of the solar spectrum (Supplementary Fig. 14a).

In conclusion, we have presented here a method to extract the photogeneration yield spectrum of mobile charge carriers from optical and EQE measurements. It is similar to IQE measurements, but crucially relies both on precise optical modelling to isolate the optical generation only in the active photoabsorber layer under operating conditions, and on the thickness of this layer being small enough not to be distorted by spatially varying optical and charge transport and recombination effects. We applied this method to the study of an ultrathin (7 nm) haematite photoanode under operando PEC conditions, and the results obtained were found consistent for front and back illuminations and showed agreement with the photoconductivity action spectrum obtained from TRMC measurements of a thick (150 nm) haematite layer. From those results, we have provided a direct link between wavelength-dependent PEC behaviour and high-frequency photoconductivity measurements. We have also shown that the photogeneration yield of mobile charge carriers provides an upper limit for the photoconversion efficiency of haematite photoanodes that is substantially lower than that predicted by its bandgap alone. Furthermore, the results are consistent with the assignment of haematite's optical absorption spectrum to a broad LMCT band, which generates mobile charge carriers, overlayed with non-contributing ligand field excitations. As demonstrated in this work for haematite, TiO_2 and $BiVO_4$, the proposed methodology to extract the photogeneration yield spectrum can be applied to a wide range of photoabsorber materials.

Online content

Any methods, additional references, Nature Research reporting summaries, source data, extended data, supplementary information, acknowledgements, peer review information; details of author contributions and competing interests; and statements of data and code availability are available at https://doi.org/10.1038/ s41563-021-00955-y.

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Received: 10 December 2019; Accepted: 10 February 2021; Published online: 19 April 2021

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Methods

The haematite, ITO, Nb:SnO₂ (NTO) and TiO₂ depositions were performed using a turn-key PLD workstation (PLD/MBE 2100, PVD Products) equipped with a KrF pulsed excimer laser beam (λ = 248 nm, COMPex PRO 102 Excimer Laser, Lambda Physik / Coherent). The haematite films were deposited from a 1 cation% Sn-doped Fe₂O₃ target prepared in-house as described elsewhere²⁰. The ITO current collector layer for the haematite photoanode was deposited from a commercial ITO target (purity 99.99%, In₂O₃/SnO₂ ratio of 90:10, ACI Alloys). The TiO₂ ultrathin (~11 nm) film photoanode was prepared by PLD from 1 cation% Nb-doped TiO, and NTO in-house-made targets. For the spatial collection efficiency analysis, the haematite and ITO layers were deposited on an Eagle glass substrate at a set-point temperature of 500 °C and in an oxygen pressure of 25 and 10 mtorr, respectively. For the TiO₂ photoanode, the NTO current collector film was deposited at 800 °C in an oxygen pressure of 5 mtorr on a sapphire (0001) substrate. The Nb-doped TiO₂ film was deposited on top of the NTO film at 500 °C in an oxygen pressure of 25 mtorr O₂. The BiVO₄ photoanodes were prepared by PLD using a custom-built PLD system (PREVAC) equipped with a KrF pulsed excimer laser beam $(\lambda = 248 \text{ nm}, \text{LPXpro 210}, \text{Coherent})$. For film deposition, an in-house-made BiVO₄ target was used. BiVO, films were deposited at room temperature and subsequently annealed in air at 450 °C for 2 h. Further details on the $\bar{\rm BiVO_4}$ deposition are reported elsewhere48.

For the TRMC measurements, a thick (~150 nm) Sn-doped haematite layer was deposited epitaxially on a sapphire (0001) substrate at a set-point substrate temperature of 800 °C and in an oxygen pressure of 10 mtorr as described previously in more detail⁴⁹.

The transmission and reflection spectra of the ultrathin-film haematite photoanode were measured using a Cary 5000 series UV-Vis-NIR spectrophotometer (Agilent) and a Universal Measurement Accessory. The optical parameters (complex refractive index) of the haematite, ITO, $BiVO_4$, TiO_2 and NTO layers and the glass and sapphire substrates were obtained by spectroscopic ellipsometry (VASE Ellipsometer, Woollam).

Photocurrent versus wavelength measurements are commonly known as IPCE or EQE measurements. The EQE system we used was based on a modified Quantum Efficiency measurement kit (Oriel QE-PV-SI, Newport), which included a 1 kW input xenon lamp source with a Cornerstone 260 monochromator operated at a wavelength resolution of ~2 nm. The photocurrent was measured in three-electrode mode using a potentiostat (Zennium, Zahner Electrik). A wavelength-calibrated 1918-C Newport optical power meter with a high-performance ultraviolet-enhanced silicon photodiode sensor was used to normalize the photocurrent by the incident light intensity. A high-power white-light LED (Mightex Systems, 6,500 K 'glacial white' spectrum, 300 mW maximum radiant flux) was used to direct white-light bias in the order of 1 Sun intensity (1 kW m⁻²) onto the sample. By comparison, the monochromatic probe intensity was in the order of 10 W m⁻². The LED bias was applied at an oblique angle either to the front or back of the sample. Care was taken to ensure proper distances, mirror angles and lateral positions of sample and detector. To overcome both current drift and fluctuation noise problems endemic in measurements under conditions of strong white-light bias, an automated rotary mirror stage was implemented to alternately direct the monochromatized incident light toward the sample and optical power meter, so that the light current, dark current and optical power were measured within a few seconds of each other at each wavelength. The EQE measurements, including bias light intensity and potential dependence, are discussed in more detail in the Supplementary Information.

TRMC measurements were performed by mounting the samples in a microwave cavity cell and placing them within a set-up similar to the one described elsewhere⁵⁰. A voltage-controlled oscillator (SiversIMA VO3262X) generated the microwaves (X-band region, 8.4–8.7 GHz). During the measurements, the change in the microwave power ($\Delta P/P$) reflected by the cavity upon sample excitation with 3 ns (full-width at half-maximum) pulses of a wavelength-tunable optical parametric oscillator coupled to a diode-pumped

Q-switched Nd:YAG laser at wavelengths between 405 and 590 nm (5 nm steps, 50 Hz repetition rate) was monitored.

Data availability

The authors declare that the data supporting the findings of this study are available within the paper and its Supplementary Information files.

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Acknowledgements

D.S.E., D.A.G. and Y.P. acknowledge G. Ankonina for generously assisting on technical matters whenever needed in the Technion's Photovoltaics Laboratory, and also A. Inbar for assisting in the EQE measurements in this work. We thank G. Atiya for the TEM measurements, L. Popilevsky from the FIB Lab at the Technion's Russell Berrie Nanotechnology Institute (RBNI) for preparing the TEM sample, and J. N. Hilfiker from J. A. Woollam Co. for helpful correspondence regarding ellipsometry analysis. The research leading to these results received funding from the PAT Center of Research Excellence supported by the Israel Science Foundation (grant no. 1867/17). The EQE and optical measurements were carried out at the Technion's Photovoltaics Laboratory (HTRL), supported by the RBNI, the Nancy and Stephen Grand Technion Energy Program (GTEP) and the Adelis Foundation. Part of this research was carried out within the Helmholtz International Research School 'Hybrid Integrated Systems for Conversion of Solar Energy' (HI-SCORE), an initiative co-funded by the Initiative and Networking Fund of the Helmholtz Association. Part of the work was funded by the Volkswagen Foundation. D.A.G. acknowledges support from the Center for Absorption in Science of the Ministry of Aliyah and Immigrant Absorption in Israel. Y.P. acknowledges support by GTEP and for a Levi Eshkol scholarship from the Ministry of Science and Technology of Israel. A.R. acknowledges the support of the L. Shirley Tark Chair in Science.

Author contributions

D.A.G. and H.D. conceived the idea and initiated the research. D.A.G., D.S.E. and Y.P. developed the methodology for the ultrathin-film spatial collection efficiency analysis. D.A.G., Y.P. and P.S. fabricated the haematite, $BiVO_4$ and TiO_2 photoanodes. Y.P. performed the ellipsometry analysis. D.S.E. designed the EQE experiment. M.K., D.F., E.F.A. and D.A.G. designed the TRMC experiments with the help of R.v.d.K., D.A.G., D.S.E., Y.P., M.K., D.F. and A.K. performed the characterizations and data analysis. D.A.G. and D.S.E. wrote the first draft of the manuscript. A.R. supervised the project. All authors contributed to the scientific discussion and editing of the manuscript.

Competing interests

The authors declare no competing interests.

Additional information

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