

Quantifying the Photoelectrochemically Active Surface Area for Oxygen Evolution Metal Oxide Photoelectrocatalysts

Camilo A. Mesa,* Shababa Selim, Andreas Kafizas, Yi Wen, Victor Landgraf, Ludmilla Steier, Yimeng Ma, Miriam Regue, Dongho Lee, Mikel F. Hurtado, Salvador Eslava, Sixto Gimenez, Kyoung-Shin Choi, Laia Francàs,* and James R. Durrant*



Cite This: <https://doi.org/10.1021/acscatal.6c01573>



Read Online

ACCESS |



Metrics & More



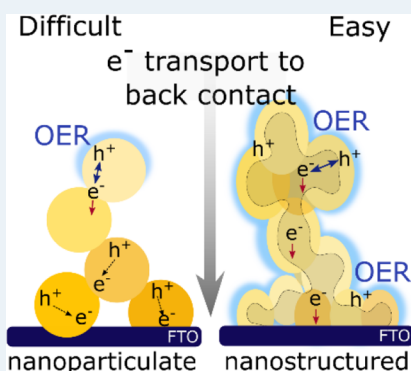
Article Recommendations



Supporting Information

ABSTRACT: Nanostructuring is established as a photoelectrode performance enhancing route for solar-driven catalytic processes. However, it is often unclear to what extent the increase in photoelectrode physical surface area directly results in a commensurate increase in photoelectrochemically active surface area. While there are established methods for estimating the physical and electrochemically active surface areas, it is challenging to quantify the *operando* photoelectrochemically active surface area of nanostructured or nanoparticulate photoelectrodes. Herein, we demonstrate that photoinduced absorption (PIA) spectroelectrochemistry can be employed to quantify the *operando* photoelectrochemically active area of photoanodes for the oxygen evolution reaction (OER) by exploiting the strong dependence of OER turnover frequency on physical surface hole density. We investigate BiVO₄, α -Fe₂O₃, and TiO₂ photoanodes with contrasting morphologies – planar, nanoparticulate, and nanostructured. Our study combines *operando* measurements of TOF and geometric surface hole density to quantify the photoelectrochemically active surface area of each catalytic system for OER. For the nanostructured photoelectrodes, the photoelectrochemically active surface areas determined from our PIA analyses are shown to be in agreement with their physical surface area, consistent with their good OER performance. This contrasts with the low photoelectrochemically active surface areas compared to their high physical surface area determined by the nanoparticulate photoelectrodes, resulting in poor performance. We conclude by demonstrating how the photoelectrochemically active surface areas of nanoparticulate photoelectrodes increase when driving more kinetically facile reactions or by adding co-catalysts.

KEYWORDS: *operando* spectroelectrochemistry, photoelectrochemically active surface area, effectiveness of nanostructuring, oxygen evolution, metal oxide photoanodes



1. INTRODUCTION

Photoelectrochemical water splitting has been widely studied over the last decades as a means to generate solar-driven chemical fuels such as hydrogen.^{1–3} Metal oxides are receiving particular attention as photoanode materials for the kinetically and thermodynamically challenging water oxidation reaction.⁴ For such metal oxide photoanodes, highly nanostructured electrodes with large surface areas have often been favored to facilitate surface catalysis.^{5–7} A high surface area to volume ratio can increase the yield of photogenerated charges that can access the exposed surface with the electrolyte and can thus suppress bulk recombination losses.^{8–10} For example, nanostructured electrodes of hematite (α -Fe₂O₃), titania (TiO₂), and WO₃/BiVO₄ heterojunctions have been shown to exhibit enhanced photocurrents for water oxidation catalysis relative to flat electrodes without the need for added electrocatalysts.^{11–17} However, increasing photoelectrode surface area does not always lead to enhanced catalytic performance for water oxidation.¹⁸ For example, nanoparticulate, mesoporous titania

(TiO₂), and bismuth vanadate (BiVO₄) photoelectrodes have shown lower photocurrents than flat photoelectrodes, unless functionalized with surface co-catalysts (such as Co-FePB and Fe/Ni oxyhydroxides).^{19,20} The strong performance enhancement observed with the addition of co-catalysts to such nanoparticulate electrodes suggests that in the absence of added co-catalysts, a large proportion of the surface is inactive for photoelectrochemical water oxidation catalysis. It has been suggested that this may result from the slow water oxidation catalysis being unable to compete effectively with surface (or “back electron–hole”) recombination losses in such nanoparticulate electrodes.²¹ This is consistent with the high performance

Received: February 27, 2026

Revised: June 30, 2026

Accepted: July 1, 2026

for such nanoparticulate electrodes for the catalytic oxidation of hole scavengers such as sulfite and methanol.^{20,22} As such, a key challenge is to determine the design requirements for nanostructured photoelectrodes to obtain efficient performance toward OER catalysis and, in particular, the extent to which the higher physical surface area generated by nanostructuring also increases the catalytically active surface area.

The surface roughness factor (R_F) is often used as a metric for quantifying the surface area of photoelectrodes. Three different methods are typically employed to determine the physical surface area of photoelectrodes: N_2 adsorption–desorption isotherms using Brunauer–Emmett–Teller (BET) analysis, atomic force microscopy (AFM), where R_F can be readily calculated from the surface map, and dye adsorption, where an adsorbed probe molecule is quantified upon desorption and a corresponding surface area is approximated. These methods are collectively referred to here as determining R_F^{phys} . Due to the nature of these R_F^{phys} quantifications, BET tends to overestimate the active surface area since the measurement is not performed on the electrode and N_2 can diffuse and adsorb where the electrolyte cannot reach, while AFM and dye adsorption could underestimate the active area due to the size of the AFM tip and dye molecule, respectively. Alternatively, the electrochemically active surface area (R_F^{EC}), measured by the double-layer capacitance (C_{DL}) or underpotential deposition (UPD) of metals, has been used to analyze electrocatalytic systems. The C_{DL} method involves comparing the C_{DL} ^{23,24} with the specific capacitance (C_s) of a planar electrode, with the relationship defined as $R_F^{\text{EC}} = C_{\text{DL}}/C_s$. The UPD method is based on the electrochemical quantification of the adsorption charge (Q_{nano}) of foreign metals such as lead and comparing it with that for planar electrocatalysts (Q_{planar}).²⁵ These methods are limited by C_s generally not being well characterized for photoelectrode materials and Q_{nano} commonly characterized on single crystal electrodes. Moreover, while these methods provide the physical and electrochemically active areas of photoelectrodes, they do not necessarily correspond to the active surface area driving photoelectrochemical catalytic water oxidation.^{26,27} In particular, such analyses do not take into account the impact of kinetic competition between surface recombination and catalysis in limiting the effective photoelectrochemically active surface area, R_F^{PEC} .

A particular concern for water oxidation photoelectrocatalysis on metal oxides is the kinetic mismatch between bulk charge carrier lifetimes (ps–ns in most metal oxides) and the timescale of water oxidation catalysis (typically seconds).^{28,29} In most photoanodes, the accumulation of sufficiently long-lived surface holes to drive catalytic water oxidation is enabled by the formation of a surface space charge layer (SCL).^{30–32} However, the length scale of this SCL typically ranges from tens to hundreds of nanometers. This thickness is often insufficient for metal oxides to effectively capture light at or near the band edge unless they are appropriately nanostructured.²⁶ In the study herein, we propose an operando spectroelectrochemical assay of the photoelectrochemically active surface area, R_F^{PEC} . This assay is shown to be an effective predictor of photoelectrode performance and provides new insights into the impact of photoelectrode nanostructuring on photoelectrochemical (PEC) performance.

The study herein focuses on the determination of the photoelectrochemically active surface area driving water oxidation

catalysis R_F^{PEC} for planar, nanoparticulate, and nanostructured photoanodes employing three of the most studied metal oxides for water oxidation, namely, BiVO_4 , $\alpha\text{-Fe}_2\text{O}_3$, and TiO_2 . The studies carried out herein are particularly focused on unraveling the relationship between nanostructuring, charge accumulation, and photoelectrochemical activity for water oxidation catalysis. Using *operando* spectroelectrochemical photoinduced absorption spectroscopy (PIAS), we directly quantify the density of surface accumulated holes. In such PIAS studies, we monitor the transient UV–Vis absorption changes (i.e., the differential optical density, ΔOD) of the photoelectrode induced by an LED light pulse of typically 5 s duration as a function of light intensity (typically from 0.01 to circa 2 suns equivalent) or applied potential. The 5 s duration is selected to achieve the quasi-steady state accumulation of reactive species, i.e., surface holes for OER or organic transformations on photoanodes, with the measured change in ΔOD being directly proportional to the density of these species.³³ This measured surface hole density corresponds to holes that have reached the surface overcoming bulk recombination and trapping processes. The ability of PIA spectroscopy to quantify the *operando* density of accumulated surface holes as a function of operating conditions (light intensity, bias, etc.) is a key feature of this technique. Comparison of this surface hole density with the simultaneously measured photocurrent density allows quantification of the reaction kinetics.^{34,35} Our initial PIA studies of water oxidation kinetics on metal oxide photoanodes concluded that the density, and thus the coverage, of surface holes was the main driving force for water oxidation catalysis,^{36,37} with the reaction rate exhibiting rate law dependence on surface hole density.^{38–40}

$$j^{\text{ph}} = k_{\text{OER}} \cdot [h^+]^{\alpha} \quad (1)$$

where α is the order of the reaction with respect to the surface hole density $[h^+]$, k_{OER} is the observed OER rate constant, and j^{ph} is the measured photocurrent. Such rate law behavior has now been confirmed both experimentally by a range of techniques and through DFT/microkinetic modeling.^{34,41,42} OER on metal oxides under circa 1 sun irradiation is typically observed to be third order in hole density. We, and others, have previously employed PIA spectroscopy to study the rate law kinetics of water oxidation, methanol oxidation, and proton reduction across metal oxide photoelectrodes of varying structure.^{22,36,37,43,44}

The densities of surface holes measured by PIAS and also by impedance spectroscopy (EIS)^{42,45} are in the order of $10^{14} \text{ h}^+ \text{ cm}^{-2}$, significantly higher than the surface defect densities typically reported for such metal oxide photoanodes (10^{12} – 10^{13} cm^{-2}),^{42,45} supporting theoretical analyses, which indicate that OER on metal oxides does not require surface defects (e.g., lattice dislocations, etc.)⁴¹ and is therefore likely to be relatively independent of surface defect densities. This conclusion is supported experimentally by the observation that for hematite photoanodes, the spectral fingerprints of surface holes, OER rate constant k_{OER} , and reaction order α are invariant between photoanodes with different morphologies and defect densities.⁴⁶ As such, it appears that the primary determinants of OER reaction kinetics on metal oxide photoanodes are the choice of metal oxide and the density of valence band holes accumulated on its surface.^{22,37–41,46}

In the study herein, we exploit the nonlinear dependence of OER photocurrent density upon surface hole density, which results in the OER turnover frequency depending strongly upon surface hole density. As such, measurement of the turnover frequency for a photoanode can be employed to determine its effective surface hole densities and thereby determine its photoelectrochemically active surface area. We contrast this PIA based measurement of R_F^{PEC} to the measured physical surface roughness of a range of photoanodes. This approach is first employed to compare R_F^{PEC} between planar and highly active nanostructured photoanodes, where we find $R_F^{PEC} \sim R_F^{phys}$, confirming the validity of our approach and its underlying assumptions. We then go on to investigate less active nanoparticulate photoanodes, where we find $R_F^{PEC} \ll R_F^{phys}$, thereby providing quantitative insight into the factors limiting their lower activity for OER. The results obtained herein thus can help guide the design of efficient photoelectrodes, when considering nanostructuring to maximize the surface usage for catalysis. They also shed light on the instances when the addition of surface electrocatalysts can be beneficial, particularly when increasing the surface area of the photoelectrocatalyst alone is found to be ineffective.

2. RESULTS AND DISCUSSION

2.1. Photoelectrode Physical and Photoelectrochemical Characterization toward the Oxygen Evolution Reaction (OER)

In this study, we compare the photoelectrochemical OER catalysis of planar, dense photoelectrodes (pl) with two “nanostructured” (ns) and two “nanoparticulate” (np) photoelectrodes of $\alpha\text{-Fe}_2\text{O}_3$, TiO_2 , and BiVO_4 . The fabrication and structural and optical characterization of these photoelectrodes have been reported previously, with relevant details, SEM images, and XRD characterization provided in Figure 1a and Figures S1–S5.^{20,47–53} Physical and electrochemically active surface areas for the studied films have previously been determined using a range of methodologies (BET, AFM, dye adsorption, and/or dark electrochemically active surface area measurements). These surface areas are quantified as physical and electrochemical film roughness factors, R_F^{phys} and R_F^{EC} , respectively (see Table 1 and refer to Supporting Information Section 4 for R_F determination details and further discussion). Figures 1a and S2 specifically compare the cross-section (insets: top view) SEM images of the studied pl- TiO_2 (top), np- TiO_2 (middle), and ns- TiO_2 (bottom) photoanodes, exhibiting planar, nanoparticulate, and nanostructured morphologies, respectively. The pl- TiO_2 films are composed of crystallites with sizes $\sim 50\text{--}200$ nm, compared to the spherical nanoparticles of ~ 20 nm diameter exhibited by the np- TiO_2 photoanode. The pl- BiVO_4 films are ~ 450 nm thick and are composed of crystallites with sizes $\sim 50\text{--}200$ nm, while the np- BiVO_4 films are $\sim 450\text{--}500$ nm thick with an average particle size of 76 nm. The ~ 20 nm thick pl- $\alpha\text{-Fe}_2\text{O}_3$ photoanodes present a flat and ordered structure, while the ns- $\alpha\text{-Fe}_2\text{O}_3$ films are ~ 500 nm thick and composed of dendrites/cauliflowers of $75\text{--}250$ nm width (see Figures S3 and S4). All pl- photoelectrodes exhibit R_F^{phys} values close to 1 as expected for dense, planar films (see Figures S1, S3, and S6 and Table 1), while the nanoparticulate, np- TiO_2 and np-

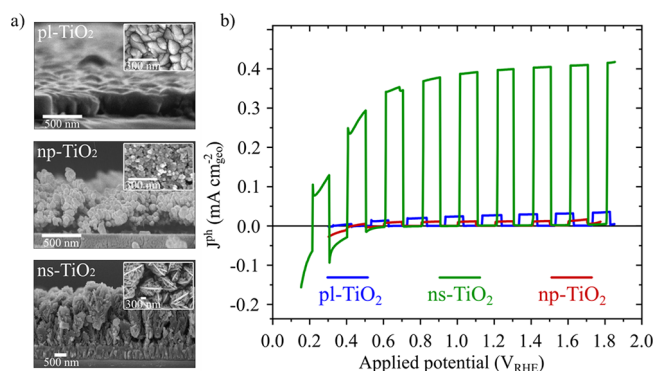


Figure 1. Physical and photoelectrochemical characterization of TiO_2 photoanodes toward OER activity. (a) SEM micrographs of the planar, pl- (top panel), nanoparticulate, np- (middle panel), and nanostructured, ns- (bottom panel) TiO_2 photoanodes (see micrographs comparing these structures with the same scale bar in Figure S2). (b) Curves of photocurrent density (J^{ph}) vs applied potential for the pl- (blue), np- (red), and ns- (green) TiO_2 photoanodes, normalized by geometric area (cm^{-2}), under 355 nm front illumination conditions in 1 M NaOH. J^{ph} for the ns- vs the np- TiO_2 film is one order of magnitude larger.

BiVO_4 , show R_F^{phys} of 120 and 20, respectively. Interestingly the ns- TiO_2 shows a nanoplate, rose-like nanostructure, similar to the nano-cauliflower ns- $\alpha\text{-Fe}_2\text{O}_3$ photoanode also studied herein (see Figure 1a, bottom and Figure S4c), featuring $R_F^{EC} = 28$ ⁴⁹ and $R_F^{phys} = 21$,⁵⁰ respectively. Considering that these films comprise thicknesses between 300 nm up to 2 μm , it is apparent from Figures 1a and S2 that their physical surface areas, thus R_F^{phys} , differ significantly. We consider next the correlation between the observed photocurrents and these differing R_F^{phys} .

First, all the prepared samples were tested for water oxidation catalysis, a challenging and slow reaction, since it involves the formation of an oxygen–oxygen double bond and the removal of 4 electrons and 4 protons from two water molecules. The resulting $J\text{--}V$ curves for TiO_2 are shown in Figure 1b, and for $\alpha\text{-Fe}_2\text{O}_3$ and BiVO_4 in the Supporting Information (Figure S7a,b, respectively). Note that the presented $J\text{--}V$ curves and the subsequent analysis in Figure 1 were performed normalizing the photocurrent by the geometric surface area. As can be observed in Figure 1b, the ns- TiO_2 exhibits one order of magnitude higher photocurrent than the pl- TiO_2 analogue. This trend is also found when comparing ns- $\alpha\text{-Fe}_2\text{O}_3$ with pl- $\alpha\text{-Fe}_2\text{O}_3$ photoanodes (Figure S7a), coinciding in both cases, in terms of order of magnitude, with the observed increase in R_F^{phys} in Table 1. However, in contrast to the one order of magnitude higher R_F^{phys} encountered for both np- TiO_2 and np- BiVO_4 with respect to their pl- counterparts, both nanoparticulate

Table 1. Physical Roughness Factors (R_F^{phys}) of the pl-, np-, and ns- Photoelectrodes

structure	film	R_F^{phys}	film	R_F^{phys}	film	R_F^{phys}
planar	pl- TiO_2	1.35	pl- Fe_2O_3	1.20 ⁵²	pl- BiVO_4	1.02
nanostructured	ns- TiO_2	28	ns- Fe_2O_3	21 ⁵⁰	np- BiVO_4	20 ⁵⁵
nanostructured	np- TiO_2	120 ⁵⁴				

photoelectrodes yielded low water oxidation photocatalytic currents, even lower than their planar equivalents ($\sim 60\%$ lower J^{ph}). More specifically, measured at 1.5 V vs RHE, for TiO_2 , the np- film reaches $12 \mu\text{A cm}^{-2}$ compared to $30 \mu\text{A cm}^{-2}$ shown by the pl- photoelectrode; for BiVO_4 , the np- film shows 0.39 mA cm^{-2} , compared to 1.19 mA cm^{-2} exhibited by the pl- counterpart (Figures 1b and S7b). To start rationalizing these results, we move to study the intrinsic OER kinetics of the herein reported photoelectrodes.

2.2. Intrinsic OER Activity Determination

Given the mismatch in the measured physical area and the PEC performance of the np- films, we turn to use *operando* spectroelectrochemical photoinduced absorption spectroscopy (PIAS) to determine the intrinsic OER catalytic activity in terms of turnover frequencies (TOF) vs surface hole density (per geometric area, i.e., without considering the roughness factor) on our photoelectrodes. In PIAS, we employ optical absorption spectroscopy to quantify the accumulation of surface holes under steady-state conditions of photoelectrochemical reactions, in particular water oxidation catalysis in this work.³⁶ This approach can be applied when the photoelectrocatalytic activity follows a population driven kinetics, where the rate of the catalytic reaction depends on the concentration of reactive species, assuming an invariant rate constant under catalytic conditions (see eq 1). The validity of this methodology and assumption is discussed below. Typically, such measurements are performed as a function of light intensity under a constant applied anodic potential. The resulting surface hole density (h^+) and the corresponding steady-state photocurrent density (J^{ph}) corresponding to the oxygen evolution reaction rate can, upon reorganizing eq 1, be fitted according to the equation:

$$\text{TOF} = \frac{J^{\text{ph}}}{[h^+]} = k_{\text{OER}} [h^+]^{\alpha-1} \quad (2)$$

where TOF is the turnover frequency per surface hole (i.e., the inverse of their decay times). This experimental approach has been reported previously by our group and others,^{55–58} where for the metal oxides studied herein, water oxidation was observed to proceed via a reaction order (α) of three under technologically relevant irradiation conditions.^{28,41,42,59} The validity of this analysis lies in the increasing evidence, in $\alpha\text{-Fe}_2\text{O}_3$ and TiO_2 , of a surface hole population-controlled OER rate at surface hole coverages (θ) below $\theta = 1$.^{41,60} In this regime, before surface hole saturation, the observed k_{OER} has been shown to be constant in $\alpha\text{-Fe}_2\text{O}_3$ photoanodes,⁴⁶ as further discussed below. The potential of such rate law behavior as a tool to study the photoelectrochemically active surface areas is discussed further below. Herein, we exploit the dependence of TOF on physical surface hole density, as detailed in eq 2, to allow us to determine this physical surface hole density from measurement of the catalytic water oxidation TOF. Comparison of this physical surface hole density with the measured geometric surface hole density determined directly from our optical data allows us to determine the photoelectrochemically active surface area R_F^{PEC} .

First, PIAS was used to monitor the optical absorption of surface holes performing OER, focusing on the TiO_2 photoelectrodes at matched TOFs, followed by a TOF analysis below. It is apparent from Figure 2a that at a matched TOF $\sim 0.7 \text{ s}^{-1}$ (obtained by varying the light intensity until we

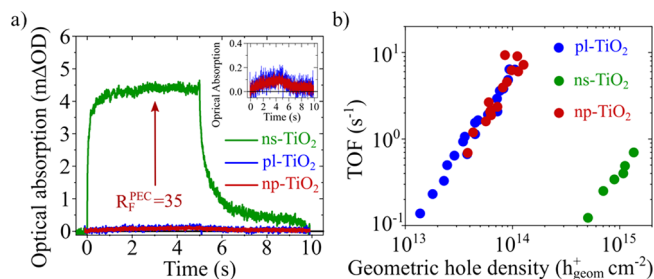


Figure 2. Intrinsic OER kinetic activity determination. (a) Typical photoinduced optical absorption (PIA) data for the np- TiO_2 (red), pl- TiO_2 (blue), and ns- TiO_2 (green) films at matched OER TOFs (0.7 s^{-1}) in 1 M NaOH. The steady-state differential optical absorption ($m\Delta\text{OD}$) of accumulated holes on the ns- TiO_2 (green) film is 35-fold higher than its planar and nanoparticulate (blue and red) analogues, thus $R_F^{\text{PEC}} = 35$. (b) Oxygen evolution turnover frequency (TOF) as a function of the geometric surface hole density h_{geom}^+ for the pl- (blue), np- (red), and ns- (green) TiO_2 photoanodes. Measurements performed under 355 nm front illumination conditions in 1 M NaOH. For a matched TOF, the np- TiO_2 film is able to accumulate 35-fold larger h_s^+ compared to its ns- and pl- counterparts.

achieve this TOF value), the density of surface holes on the ns- TiO_2 , measured by the amplitude of our PIAS signal, is *c.a.* one order of magnitude larger compared to the pl- TiO_2 photoelectrode. This observation correlates with the increased R_F^{phys} and J^{ph} shown in Figure 1 and discussed above. In contrast, the density of holes, per surface geometric area, accumulated by the np- TiO_2 photoelectrode for TOF $\sim 0.7 \text{ s}^{-1}$ (see Figure 2a, inset) appears to be almost identical to that for the pl- TiO_2 film, coinciding with their comparable photoelectrochemical behavior shown in Figure 1b. This suggests that, although the np- TiO_2 photoelectrode exhibits a larger physical surface area than the pl- TiO_2 ($R_F^{\text{phys}} = 120$, Table 1), the photoelectrochemical active surfaces of these two films are essentially the same. We can thus conclude that most of the surface of the np- TiO_2 photoelectrode is inactive for water oxidation. This is most likely due to poor electronic connectivity between particles and rapid recombination, preventing deeper regions of the film from contributing to the photocurrent. Such electronic connectivity is strongly influenced by grain boundaries and even different crystalline orientations between particles,⁶¹ affecting the np films more significantly. To confirm this conclusion, we move to combine our optical absorption measurements with the J^{ph} to determine the TOF according to eq 2 and further below in Section 2.2.2.1 (strategy 1) with the addition of a hole scavenger.

Figure 2b shows the TOF for OER on the pl-, np-, and ns- TiO_2 photoelectrodes as a function of the surface hole density per geometric area. From this figure, we can confirm that the ns- TiO_2 accumulates more holes than its nanoparticulate and planar counterparts (Figure 2b, green data) to achieve an equivalent TOF, consistent with a higher photoelectrochemical active surface area (Table 1) and its higher observed photocurrent (Figure 1b). Upon comparing ns- vs pl- $\alpha\text{-Fe}_2\text{O}_3$, a similar trend is observed in Figure S8 with the ns- $\alpha\text{-Fe}_2\text{O}_3$ photoelectrode accumulating one order of magnitude more surface holes compared to its planar counterpart, correlating with the increased R_F^{phys} and J^{ph} shown in Figure S7. This contrasts with the observation that the np- BiVO_4 accumulates a ~ 4 -fold higher density

of surface holes compared to the pl-BiVO₄ photoelectrode but produces 60% lower photocurrent, suggesting poor usage of the available surface area in bare np-BiVO₄ photoanodes (see Figures S7 and S8 and associated discussion). This effect is more severe in TiO₂, where both np- and pl-TiO₂ photoelectrodes accumulate very similar surface hole densities per geometric surface area (red and blue data in Figure 2b) to achieve the same TOF values. This validates our optical absorption measurements as well as confirms our hypothesis that only a fraction of the np-TiO₂ photoelectrode surface is useful for OER catalysis. The underlying processes responsible for such low OER activity of these np- photoelectrodes is discussed further below. From these observations in different photoelectrodes with diverse morphologies, it is apparent that (i) a more appropriate method to assess the photoelectrochemically active surface area (R_F^{PEC}) is required and (ii) strategies to increase the photoelectrodes surface usage must be discussed.

2.2.1. Determination of Photoelectrochemically Active Surface Area (R_F^{PEC}). From the previous discussion, it is clear that, to accurately determine the intrinsic activity of different photoelectrodes, it is necessary to assess the photoelectrochemically active surface area. In this work, for the first time, we use PIAS to estimate the photoelectrochemically active surface area, R_F^{PEC} , for each photoelectrode by monitoring the catalytic TOF for OER as a function of the optically determined density of surface holes. This approach exploits the nonlinear dependence of the TOF for OER on surface hole density to determine R_F^{PEC} , as detailed below.

Our PIAS measurements yield the hole density per geometric area (h_{geom}^+) as a function of light intensity during OER. This can be related to the hole density per photoelectrochemically active area (h_{PEC}^+) by the photoelectrochemically active roughness factor (R_F^{PEC}) as:

$$h_{\text{PEC}}^+ = \frac{h_{\text{geom}}^+}{R_F^{PEC}} \quad (3)$$

Consequently, employing the rate law dependence of OER kinetics reported previously:^{36,59}

$$\text{TOF} = k_{\text{OER}} \cdot [h_{\text{PEC}}^+]^{\alpha-1} = k_{\text{OER}} \cdot \left[\frac{h_{\text{geom}}^+}{R_F^{PEC}} \right]^{\alpha-1} \quad (4)$$

Equation 4 can be written for nanostructured/nanoparticulate and planar film electrodes as follows:

$$\text{TOF}_{\text{nano}} = k_{\text{OER,nano}} \cdot \left[\frac{h_{\text{geom,nano}}^+}{R_{\text{F,nano}}^{PEC}} \right]^{\alpha-1} \quad (5)$$

$$\text{TOF}_{\text{pl}} = k_{\text{OER,pl}} \cdot [h_{\text{geom,pl}}^+]^{\alpha-1} \quad (6)$$

where for planar photoelectrodes, we approximate their $R_{\text{F,pl}}^{PEC}$ by assuming that the photoelectrochemically active area is the same as the physical area, such that $R_{\text{F,pl}}^{PEC} = 1$, considering $R_F^{\text{phys}} \sim 1$ according to Table 1.

For hematite photoanodes, the observed water oxidation rate (k_{OER}) has been shown to be independent of nanostructuring and, therefore, $k_{\text{OER,pl}} = k_{\text{OER,nano}}$.⁴⁶ We would like to note that

this invariance of k_{OER} between hematite samples was observed previously⁴⁶ despite differences in the bulk crystalline structure of these films and more marked differences in their defect densities. Applying this assumption to the other photoanodes employed herein (see caveats and further discussion below), we can divide eqs 5 and 6 and, rearranging, obtain a simple expression of $R_{\text{F,nano}}^{PEC}$ as a function of geometrical hole densities and TOFs as follows:

$$R_{\text{F,nano}}^{PEC} = \frac{h_{\text{geom,nano}}^+ \cdot \text{TOF}_{\text{pl}}^{1/\alpha-1}}{h_{\text{geom,pl}}^+ \cdot \text{TOF}_{\text{nano}}^{1/\alpha-1}} \quad (7)$$

For the working conditions of matched TOFs (i.e., employing light intensities such that the planar and nanostructured electrodes exhibit matched TOFs), this equation further simplifies to:

$$R_{\text{F,nano}}^{PEC} = \frac{h_{\text{geom,nano}}^+}{h_{\text{geom,pl}}^+} \quad (8)$$

Note that this analysis, from eqs 4–7, only works for $\alpha > 1$, i.e., for catalytic reactions that are nonlinear in surface hole density, such as those which require the interaction of more than 1 surface hole to reach the transition state and overcome the rate determining step, such as methanol, ethanol, or water oxidation.^{22,36,37,43,58}

We turn now to the quantitative determination of the photoelectrochemically active area $R_{\text{F,nano}}^{PEC}$ for the nanoparticulate and nanostructured photoanodes studied herein and how these compare to measurements of their physical/electrochemically active surface areas R_F^{phys} and R_F^{EC} . For all the photoanodes studied herein, the observed rate law behavior presented $\alpha \sim 3$ over the light intensity ranges studied (i.e., third order behavior in surface hole density, see Figures 2b and S8). From these data, comparing the amplitude of the optical signals, eq 8 was employed to determine $R_{\text{F,nano}}^{PEC}$ (red bars), which can be compared with those for R_F^{phys} (yellow bars) in Figure 3. This figure contrasts the values of $R_{\text{F,nano}}^{PEC}$ for the ns-TiO₂ with the pl-TiO₂ (green vs blue data in Figure 2a,b), for which an increase factor, $R_{\text{F,nano}}^{PEC}$, of 35 is found. This value of $R_{\text{F,nano}}^{PEC}$ appears to be in good agreement with the R_F^{phys} (21 and 28,⁴⁹ yellow bars in Figure 3) values measured by dye adsorption and ECSA, respectively. Similarly, for the ns- α -Fe₂O₃, the determined $R_{\text{F,nano}}^{PEC}$ of 21 coincides with the dye adsorption R_F^{phys} reported previously,⁵⁰ see Figure 3a. This agreement further confirms that k_{OER} is independent of film nanostructuring, as discussed above, and thus validates our analysis.

This close agreement between $R_{\text{F,nano}}^{PEC}$ and R_F^{phys} in nanostructured electrodes indicates that essentially all of the physical surface areas of the AACVD and APCVD films, i.e., ns-TiO₂ and ns- α -Fe₂O₃, are photoelectrochemically active for water oxidation catalysis. This conclusion is consistent with the high photoelectrochemical water oxidation performance of these electrodes (Figure 1b). This agreement supports the validity of our analysis and specifically our assumption, as discussed above, that the catalytic water oxidation TOF is primarily dependent on *operando* surface hole density and independent

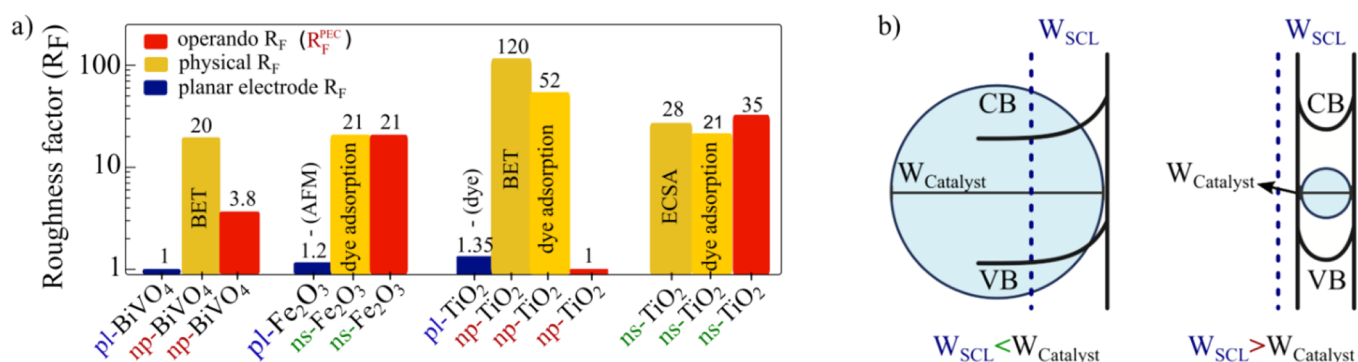


Figure 3. Benchmarking of the physical surface area and the *operando* surface usage for water oxidation. (a) Bar chart showing the differences in the physically determined R_F using BET (ochre), dye adsorption (yellow), and ECSA (ochre) methods, and the observed $R_{F,nano}^{PEC}$ (red) determined in *operando* for water oxidation. (b) Schematic representation of the effect of particle size in band bending formation compared to space charge layer (SCL) width.

of the photoelectrocatalyst morphology, as further discussed below.

In contrast, for the nanoparticulate photoelectrodes, np-TiO₂ and np-BiVO₄, a significant mismatch between their $R_{F,nano}^{PEC}$ and R_F^{phys} is evident from Figure 3a. In particular, for the np-BiVO₄ photoelectrode, the encountered $R_{F,nano}^{PEC}$ (3.8) is ~5-fold smaller than the reported R_F^{phys} (20).⁵⁵ This reduced $R_{F,nano}^{PEC}$ vs R_F^{phys} is even more pronounced (1–2 orders of magnitude difference, depending on the R_F^{phys} determination method) in np-TiO₂ exhibiting a $R_{F,nano}^{PEC}$ of 1 compared to the measured (52 by dye adsorption) or reported (120 by BET⁵⁴), R_F^{phys} values. One hypothesis for such a mismatch is the possible overestimation of the area in contact with the electrolyte by physical methods such as BET, given that BET requires a sample preparation that removes the nanoparticles from the photoelectrode and uses N₂ (a small molecule) for the adsorption–desorption isotherms.¹⁸ On the other hand, methods such as electrochemical surface area (ECSA) might result in misestimations if not performed properly,⁶² and dye-adsorption usually uses dye molecules that could be larger than the pore sizes of the studied nanostructures. In particular, from our observations, we can conclude that the dye adsorption method provides a good approximation of the available surface area for OER catalysis in nanostructured photoelectrodes (ns-TiO₂ and ns- α -Fe₂O₃), based on the good match of $R_{F,nano}^{PEC}$ and R_F^{phys} . However, for np- films, we can conclude that the dye adsorption method cannot accurately quantify the photoelectrochemically active surface area. This is most likely due to the accessibility of the electrolyte, and thus dye, within the large pores between the nanoparticles through deep layers of the photoanodes. However, as discussed previously, due to poor electronic connectivity and increased recombination, such deeper layers of the np-TiO₂ are inactive for OER. For the case of the np-TiO₂ photoelectrode, the implication of our results is that, given $R_{F,nano}^{PEC} \ll R_F^{phys}$, only a fraction layer is active for photoelectrochemical OER as $R_{F,nano}^{PEC} = 1$, most likely because these physical methods do not account for recombination losses in photoelectrodes under working conditions, as discussed further below.

Our analyses are based on an assumption of $k_{OER,pl} = k_{OER,nano}$ as justified above. While we cannot rule out possible small changes in k_{OER} from changes in the intrinsic interfacial kinetics and thus

deviations in our approximation, due to structural differences,^{63–65} i.e., surface terminations or exposed crystal facets leading to differences in intrinsic catalytic activity, we note that the main facets ((101) and (200) for TiO₂, (104) and (110) for α -Fe₂O₃,⁶⁴ and (101), (011), and (110) for BiVO₄) reported in the XRD characterization (Figures S1–S4) of the photoelectrodes studied herein are similar. We further note that the XRD patterns in this work do not intend to represent a quantitative analysis of the exposed crystal facets, but to show their presence in all studied films. However, we would like to emphasize the excellent match between $R_{F,nano}^{PEC}$ and R_F^{phys} for both ns-TiO₂ and ns- α -Fe₂O₃ photoelectrocatalysts, independent of the different additional reported facets in our photoelectrodes. On the other hand, assuming that the mismatch between $R_{F,nano}^{PEC}$ and R_F^{phys} for the nanoparticulate photoelectrodes arises from differences in their intrinsic catalytic activity, k_{OER} would have to increase one order of magnitude for the np-TiO₂ and ~4-fold for the np-BiVO₄ photoelectrodes. Given their small differences in their XRD patterns, such striking changes appear to be unlikely. This supports our hypothesis that the changes observed in the rate law are mainly due to different PEC activities of the photoelectrocatalyst surfaces rather than nanomorphology.

Our observations herein, consistent with the literature,²⁰ indicate that in photoelectrochemical OER catalysis, the total physical or electrochemical surface area does not always match the actual photoelectrochemically active area. This is, most likely, due to the presence of recombination processes, and in particular surface recombination, occurring faster than the desired catalytic reaction.^{10,28} For example, on photoelectrodes with a space charge layer (SCL) thinner than the width/diameter of the material, charge separation is improved thanks to the development of a built-in potential (Figure 3b). This commonly takes place in planar and nanostructured photoelectrodes.^{30,49,66} Thus, the possibility of band bending leads photoelectrodes such as ns-TiO₂ to practically use all its surface area due to retarded surface recombination. In the particular case of the ns-TiO₂, this can be attributed to both the thickness of the platelets composing the nanostructures and the direct pathway for electrons to travel to the back contact of the ns-TiO₂ photoelectrodes.^{9,49}

On the other hand, on nanoparticulate photoelectrocatalysts, where the nanoparticle size is comparable to or smaller than the SCL width, these reduced dimensions impact the formation of the SCL. This leads to poor OER photocurrents mainly due to (i) the absence of band bending and (ii) added longer and more

tortuous electron extraction pathways that would lead to poor hole extraction efficiency^{67,68} and (iii) increased recombination reducing the population of surface holes to drive OER. This is due to the kinetics of surface recombination being faster than the OER catalytic kinetics.^{45,69–73} Thus, the formation of a built-in potential from the surface toward the bulk, leading to band bending, is necessary to increase electron extraction efficiency, thus aiding photogenerated holes to live long enough to be transferred and perform OER. As such, we can assign that one of the factors for the lower photocurrents exhibited by our np-BiVO₄ and np-TiO₂ photoelectrodes, compared to their planar counterparts, is the lack of sufficient band bending. We note that in dye-sensitized solar cells, which also employ equivalent np-TiO₂ films, the lack of band bending is mitigated by “holes” being accumulated on the sensitizer dye rather than the TiO₂ and by fast hole extraction by the iodide redox couple. We note that other factors may also contribute to the lower active areas of nanoparticulate films, including differences in exposed crystal facets and defect densities, poorer electronic connectivity, electrolyte pore accessibility, and more tortuous electron extraction pathways. In any case, our measurements indicate that in np-TiO₂, only the outmost layer is active, most likely due to excessive electron/hole recombination deeper in the nanoparticulate film. We note that this is not a new concept. The novelty herein lies in our quantification of this effect through our comparison of physical surface area with the *operando* photoelectrochemically active surface area.

2.2.2. Strategies to Increase the Surface Usage. Our analysis above indicates that the observed low photoelectrochemically active surface area of nanoparticulate photoanodes for water oxidation catalysis is due to the faster surface recombination in comparison to the slow OER kinetics. As such, strategies to increase the surface usage require accelerated hole transfer kinetics relative to surface recombination. Two such strategies are (1) replacing the slow OER by a faster reaction, such as the oxidation of hole scavengers (methanol and sulfite in this work, opening the window for organic molecule transformations),^{74–76} and (2) the use of a co-catalyst to reduce surface recombination due to the formation of a Schottky junction.^{29,30,55,77} We will discuss both strategies in the following sections.

2.2.2.1. Strategy 1: Replacing Water Oxidation. From the *J*–*V* characteristics shown in Figure 4a for the pl-TiO₂, we observe the following: (i) the photocurrents obtained for water oxidation are similar to those observed for methanol oxidation (scavenger), which implies that most of the holes reaching the surface participate in water oxidation; and (ii) the low magnitude of photocurrents for both methanol and water oxidation (≤ 0.04 mA cm⁻²) suggests that this planar photoelectrode performance is limited by significant bulk recombination losses.⁴⁷ In comparison, for the nanoparticulate np-TiO₂ analogue, an increase of ~30-fold in photocurrents is observed when methanol is added to the electrolyte. This is a strong indication of (i) lower bulk recombination losses in comparison to pl-TiO₂ and (ii) surface recombination being a dominant factor in limiting the performance for water oxidation on these np-TiO₂ films. In contrast, the nanostructured ns-TiO₂ performs well for both water and methanol oxidation, with a photocurrent of ~0.4 mA cm⁻², indicating lower bulk recombination and a good charge transfer at the surface, due to the generated band bending within the SCL and more efficient electron extraction.^{32,49}

Similar data were also observed for BiVO₄ and α -Fe₂O₃ films (Figure 4b and c). As for the pl-TiO₂ and ns-TiO₂ films, no significant increase in photocurrent density was observed upon addition of a hole scavenger for pl- α -Fe₂O₃, in agreement with previous reports,⁷⁸ thus indicating an equal surface usage in both reactions. In contrast, np-BiVO₄ showed a ~6-fold increase in photocurrent for scavenger oxidation relative to water oxidation, qualitatively similar to np-TiO₂ and confirming that the efficiency of both nanoparticulate films for water oxidation catalysis is severely limited by surface recombination losses. Under these scavenging oxidation conditions, these photoelectrocatalysts are able to use more of their surface area than under catalytic conditions for OER. In the case of the ns-Fe₂O₃ and pl-BiVO₄, the slight increase in the photocurrent in the presence of the hole scavenger is most likely due to the presence of mid-bandgap states, which can facilitate surface recombination despite the presence of a space charge layer.^{53,69,77,79–82}

2.2.2.2. Strategy 2: Co-Catalyst Deposition. Further evidence for the observed low photoelectrochemically active

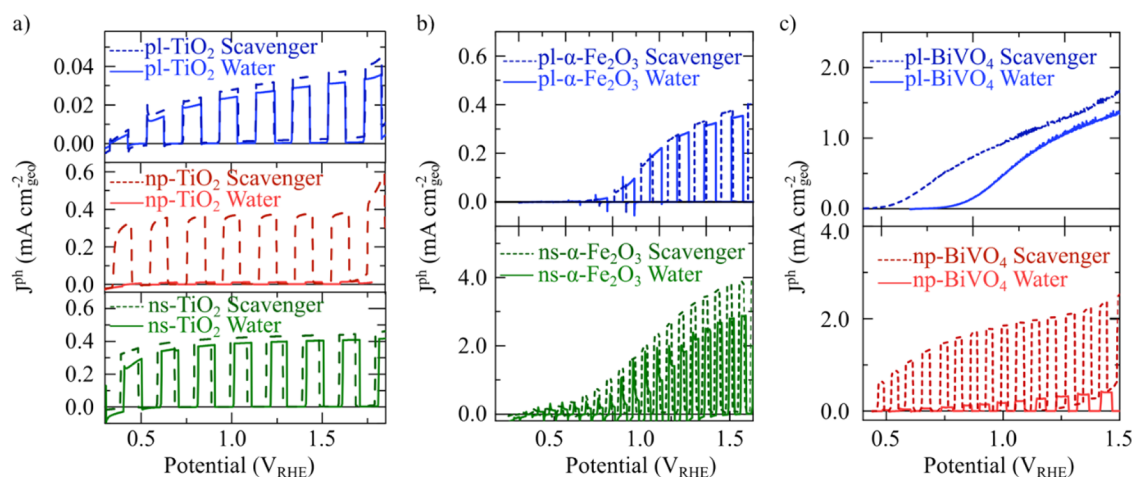


Figure 4. Effect of a hole scavenger on the PEC performance of the different photoelectrode nanostructures. j^{ph} vs *V* curves for the pl- (blue), np- (red), and ns- (green) for OER (continuous line) vs hole scavenger (dashed line) of (a) TiO₂ (OER: 1 M NaOH, pH 13.6, scavenger: 15% methanol in 1 M NaOH), (b) α -Fe₂O₃ (OER: 0.1 M NaOH, pH 13, scavenger: 95% methanol in 0.1 M NaOH), and (c) BiVO₄ (0.1 M phosphate buffer, pH 7, scavenger: 0.1 M Na₂SO₃ in 0.1 M phosphate buffer) photoanodes.

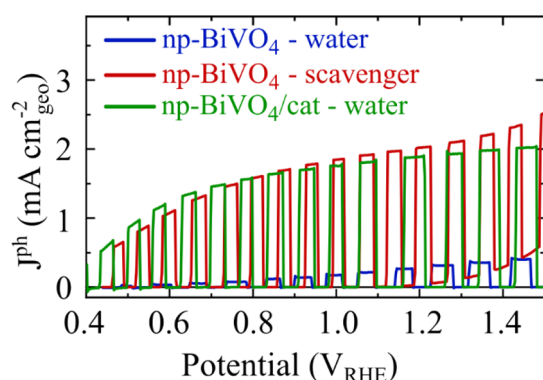


Figure 5. Effect of a co-catalyst on the PEC performance of the np-BiVO₄ photoanode. j^{ph} vs V curves for the OER (blue) in 0.1 M phosphate buffer, pH 7, scavenger (red) in 0.1 M Na₂SO₃ in 0.1 M phosphate buffer on bare np-BiVO₄ photoanodes. OER (green) in 0.1 M phosphate buffer, pH 7 on np-BiVO₄/FeOOHNiOOH photoelectrodes.

surface of nanoparticulate photoanodes for OER comes from considering the impact of co-catalyst deposition. As discussed above, for the np-BiVO₄ photoelectrode when a facile oxidation process, *i.e.*, hole transfer faster than surface recombination, such as sulfite oxidation takes place, a significant enhancement in the photocurrent is observed (Figure 5, red trace). Critically, a similar enhancement is also observed for water oxidation following deposition of a FeOOHNiOOH co-catalyst on the BiVO₄ surface, as shown in Figure 5 (green trace). This can be assigned to charge transfer to the co-catalyst, suppressing surface recombination and thus also increasing the photoelectrochemically active surface area.^{55,83}

In summary, quantifying the *operando* photoelectrochemically active surface area for a particular reaction and conditions can be a useful tool to optimize photoelectrode fabrication and performance. We have reported herein a novel methodology, based on photoinduced absorption spectroelectrochemistry (PIAS) to assess the photoelectrochemically active surface area

(R_F^{PEC}) of metal oxide photoelectrocatalysts for water oxidation. Our approach exploits the nonlinear dependence of water oxidation kinetics on effective surface hole density. Combining our kinetic assay of effective surface hole density with measurement of the geometric surface hole density (also accessible from PIAS data) and comparing to the surface hole density of flat photoelectrodes allow us to assess the photoelectrochemically active surface area R_F^{PEC} of the electrode. This allows assessment of how effective photoelectrodes are at utilizing their surface for a particular reaction/condition in photoelectrocatalysis and thus provides an assay of the effectiveness of different surface morphologies in enhancing photoelectrode performance. We conclude that adding a kinetically fast redox couple, either at the photoelectrode surface or in the electrolyte, *i.e.*, co-catalyst or hole scavenger/organic substrate, increases the R_F^{PEC} . More specifically, our data indicate that the nanostructured films studied herein, ns- α -Fe₂O₃ and ns-TiO₂ both exhibit high photoelectrochemical active surface areas of similar magnitude to their physical surface areas. This indicates that these nanostructured photoelectrodes have structural dimensions larger than the space charge layer width, W_{SCL} and thus are able to support space charge layer fields sufficient to suppress surface recombination and are thereby able to fully utilize their high physical surface areas for long lived hole accumulation to drive water oxidation catalysis. In contrast, we find that for our nanoparticulate photoelectrodes, the photoelectrochemically active surface area is much smaller than their physical surface area. This is consistent with their nanoparticle dimensions being of similar magnitude or smaller than the space charge layer width W_{SCL} . Such nanoparticle photoelectrodes are therefore likely to be depleted throughout under anodic bias,^{84,85} such that electron transport to the back contact is not spatially separated from holes accumulating on nanoparticle surfaces. This is compounded by more tortuous electron pathways, leading to more charge recombination. As illustrated in Figure 6, this contrasts with the nanostructured photoelectrodes studied herein, where their high photoelectrochemically active surface areas are indicative of electron transport to the back contact proceeding via high conductivity bulk interiors of these photoelectrodes, with their

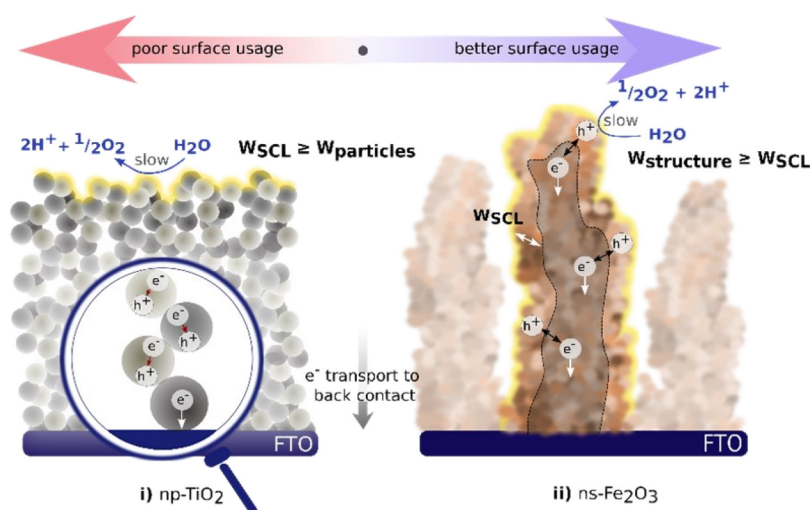


Figure 6. Schematic illustration of the effect of particle size and space charge layer width (W_{SCL}) on charge separation and overall performance. Nanoparticulate films (left) compared to nanostructured photoelectrodes (right).

space charge layer fields suppressing surface recombination between these bulk electrons and surface accumulated holes.

3. CONCLUSIONS

The studies herein demonstrate that PIA spectroscopy can be employed to quantify the photoelectrochemically active surface areas R_F^{PEC} of photoanodes for OER. The approach is based on using OER TOF as an assay of photoelectrochemical active surface hole density. For efficient nanostructured photoanodes, our assay of R_F^{PEC} is found to be in good agreement with separately measured R_F^{phys} , confirming the validity of our analytical approach, while for less efficient nanoparticulate photoanodes, R_F^{PEC} is found to be much lower than R_F^{phys} . We thus conclude that the nanostructuring length scale and connectivity to the back contact are key parameters to rationally design efficient photoelectrodes for slow surface catalytic reactions such as water oxidation. If the nanostructuring length scale is smaller than the space charge layer width, or the electronic connectivity is insufficient, the resultant photoelectrochemically active surface area can be much less than the photoelectrode physical surface area, resulting in poor photoelectrochemical performance. We have demonstrated two strategies to enhance the photoelectrochemical performance of such photoelectrodes: (1) by using a facile catalytic reaction to enhance the performance of a high surface area nanoparticulate photoelectrode, as holes do not need to be long lived on the surface before reaction; and (2) by adding a co-catalyst to aid the spatial separation of accumulated holes from electrons being transported to the back contact. We note that additional factors such as exposing active facets, light penetration depth, and modulation of doping density can further impact on the observed photocurrents but are beyond the scope of our study. The study herein highlights key design criteria for the use of nanostructuring to enhance the performance of photoelectrodes for kinetically challenging reactions such as water oxidation. Nanostructured materials with particle sizes large enough to support band bending from space charge layer formation and good electronic extraction can result in high photoelectrochemically active surface areas for OER catalytic processes even in the absence of co-catalysts. In contrast, photoelectrocatalysts with smaller particle sizes and thus higher surface areas will typically require the presence of a co-catalyst to efficiently utilize their high surface area for OER.

4. MATERIALS AND METHODS

4.1. Film Preparation

4.1.1. TiO₂. Dense, planar TiO₂ (pl-TiO₂) films were prepared using atmospheric pressure chemical vapor deposition (APCVD), following a procedure reported previously.⁴³ The films were prepared at 450 °C and annealed at 500 °C. The procedure yields relatively flat anatase films of ~300 nm thickness (see Figure 1a, as well as Figure S1a,b for SEM micrographs). The roughness factor was taken to be ~1, as seen by AFM (see reproduced data in Figure S1c).⁴³

Mesoporous nano-particulate TiO₂ (np-TiO₂) films were grown from a colloidal anatase paste on the FTO substrate, in accordance with a method reported previously.^{47,48} The films were fabricated by doctor-blading the colloidal paste using a k-bar followed by calcining at 450 °C in air for 30 min. The films were ~1 μm thick and composed of primarily spherical particles with an average particle size of ~20 nm.⁵⁴ The roughness factor of the films, as determined by BET, was ~120 (see reproduced BET analysis in Figure S1d–f for cross-section and top-view SEM micrographs, respectively).^{22,54}

Nanostructured TiO₂ films were prepared using aerosol-assisted CVD (AACVD), as detailed elsewhere.⁴⁹ The films were deposited at 500 °C for 1 h, followed by annealing at 800 °C in air. The calculation of the roughness factor using the electrochemical surface area (ECSA) is outlined in Section 2.2.1. See reproduced⁴⁹ cross-section and top-view SEM micrographs, showing a film thickness of ~2 μm, in Figure S1g,h as well as AFM top view topography in Figure S1i.

XRD patterns are reproduced and adapted in Figure S1j, and the cross-section and top-view SEM micrographs comparing the 3 films are shown in Figure 1a in the manuscript and in Figure S2 with the same magnification and bar size.

4.1.2. BiVO₄. Dense undoped BiVO₄ films were prepared using a metal–organic decomposition method reported previously.⁵³ The planar films were approximately 450 nm thick, with a roughness factor ~1 (see Figure S3a).

Nanoporous nanoparticulate BiVO₄ films were prepared in accordance with an electrodeposition method reported previously.²⁰ However, to increase the optical transmission of the films, the method was modified by decreasing the charge passed during the BiOI deposition (from 0.13 C/cm² to 0.06 C/cm²) to yield a film thickness of ~450–500 nm. The average particle width was ~76 nm as determined by SEM and ~27 nm according to the Scherrer equation (XRD).²⁰ The roughness factor of the thin, nanoporous BiVO₄ film used in this study was determined to be 20 using BET, based on the mass of BiVO₄ contained in the thin film and the specific surface area of nanoporous BiVO₄ (31.8 m²/g) reported in our previous study (see Figure S3b).²⁰ XRD patterns are reproduced in Figure S3c.

4.1.3. α-Fe₂O₃. Dense planar undoped α-Fe₂O₃ films were prepared using atomic layer deposition (ALD) at 230 °C, reported previously,⁵² annealed at 400 °C for 4 h, followed by annealing at 600 °C for 1 h. The films were of ~20 nm thickness,⁵² with a roughness factor of 1.2 determined using AFM (see Figure S4a), and the cross-section SEM micrograph is presented in Figure S4b.^{46,52}

Nanostructured silicon-doped α-Fe₂O₃ films were prepared by APCVD using a procedure detailed elsewhere.^{50,86} The films were of ~500 nm thickness, with a dendritic structure (see Figure S4c). The roughness factor of the films was determined to be ~21 using a dye-adsorption method.⁸⁷ XRD patterns are reproduced in Figure S4d.

4.2. Experimental Techniques

4.2.1. Photoelectrochemical Characterization. Photoelectrochemical (PEC) measurements were conducted in a home-built three electrode cell. The pl-, ns-, and np-TiO₂ films as well as the pl- and ns-Fe₂O₃ electrodes were characterized with monochromatic 355 nm LED illumination equivalent to 1 sun illumination from the front while the pl- and np-BiVO₄ films were illuminated through the back (see UV–Vis characterization in Figure S5). The PEC cell consisted of quartz windows (area 0.5 cm²), where the photoanode material was placed as the working electrode, a Pt mesh was utilized as the counter electrode, and a saturated KCl Ag/AgCl was employed as the reference electrode (Metrohm). Applied potentials were measured vs Ag/AgCl ($V_{Ag/AgCl}$) and were converted to applied potentials vs the reversible hydrogen electrode (RHE) using the Nernst equation:

$$V_{RHE} = V_{Ag/AgCl} + 0.059 \times pH + V_{Ag/AgCl}^0 \quad (S.1)$$

where $V_{Ag/AgCl}^0$ is the standard potential of the Ag/AgCl reference electrode in saturated potassium chloride solution (197 mV). An Autolab potentiostat (PGSTAT 101, Metrohm) was used to apply the potential to the cell, and the data were recorded with Nova software (Metrohm). A scan rate of 10 mV/s was used for linear sweep voltammograms.

4.2.2. Spectroelectrochemical Photo-Induced Absorption Spectroscopy (PIAS). current response under pseudo-steady state conditions was obtained using a method detailed in previous

publications.^{22,36,37,43,59} Briefly, the transient photocurrent (TPC) and the photoinduced absorption (PIA), upon illumination with a continuous LED light source, were recorded simultaneously at a constant applied potential where back-electron hole recombination processes are switched off (i.e., $\geq 1.5 V_{\text{RHE}}$). The change in the optical density was recorded at 500 nm for TiO_2 ,¹ 550 nm for BiVO_4 ,¹⁵ and 650 nm for $\alpha\text{-Fe}_2\text{O}_3$,³⁶ corresponding to the photogenerated holes in each photoelectrode. The optical signals were subsequently converted to the surface hole density using the molar extinction coefficient for the reactive holes, as reported previously: $640 \text{ M}^{-1} \text{ cm}^{-1}$ for $\alpha\text{-Fe}_2\text{O}_3$,³⁶ $420 \text{ M}^{-1} \text{ cm}^{-1}$ for BiVO_4 ,³⁷ and $2000 \text{ M}^{-1} \text{ cm}^{-1}$ for TiO_2 .⁴³ The TPC signals were measured using a potentiostat (Autolab PGSTAT101).

4.2.3. Atomic Force Microscopy (AFM). Topographic images of the ns- TiO_2 photoelectrode were measured by atomic force microscopy (AFM) using an Asylum Research Cypher ES (Oxford Instruments-Asylum Research, Santa Barbara, USA) in tapping mode under ambient conditions with a silicon cantilever AC160TSA-R3 (Olympus, Tokyo, Japan) with a spring constant $k = 25.4 \text{ N/m}$, resonant frequency $f = 291 \text{ kHz}$, and a tip radius of 7 nm.

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acscatal.6c01573>.

Additional figures and plots on the morphological characterization, the roughness factor determination, the photoelectrochemical characterization, PIAS data and TOF calculation; All of them supporting the discussion in the main text; The data is available through <https://doi.org/10.34810/DATA3518> (DOCX)

■ AUTHOR INFORMATION

Corresponding Authors

Camilo A. Mesa – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; Grupo de Investigación y Desarrollo en Ciencia Tecnología e Innovación – BioGRID, Sociedad de Doctores e Investigadores de Colombia, Bogotá 110111, Colombia; Present Address: Catalan Institute of Nanoscience and Nanotechnology (ICN2), CSIC, Barcelona Institute of Science and Technology, UAB Campus, 08193 Bellaterra, Barcelona, Spain; [ORCID.org/0000-0002-8450-2563](https://orcid.org/0000-0002-8450-2563); Email: camilo.mesa@icn2.cat

Laia Francàs – Departament de Química, Universitat Autònoma de Barcelona, Barcelona, Spain; Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; Present Address: Departament de Química, Universitat Autònoma de Barcelona, Barcelona 08193, Spain; [ORCID.org/0000-0001-9171-6247](https://orcid.org/0000-0001-9171-6247); Email: laia.francas@uab.cat

James R. Durrant – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom; Present Address: Department of Chemistry, University of Oxford, Oxford OX1 3TA, United Kingdom; [ORCID.org/0000-0001-8353-7345](https://orcid.org/0000-0001-8353-7345); Email: j.durrant@imperial.ac.uk

Authors

Shababa Selim – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom

Andreas Kafizas – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; The Grantham Institute, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom; [ORCID.org/0000-0002-2282-4639](https://orcid.org/0000-0002-2282-4639)

Yi Wen – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; Present Address: School of Materials Science and Engineering, Beihang University, Beijing 100191, China

Victor Landgraf – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; [ORCID.org/0000-0003-2169-6855](https://orcid.org/0000-0003-2169-6855)

Ludmilla Steier – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom

Yimeng Ma – Department of Chemistry and Centre for Processable Electronics, Imperial College London, White City Campus, London W12 0BZ, United Kingdom; Present Address: College of Chemistry and Chemical Engineering, Donghua University, 201620 Shanghai, China; [ORCID.org/0000-0002-7826-5338](https://orcid.org/0000-0002-7826-5338)

Miriam Regue – Department of Chemical Engineering and Centre for Processable Electronics, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom

Dongho Lee – Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States; Present Address: Department of Chemistry, University of Ulsan, Ulsan 44776, Republic of Korea; [ORCID.org/0000-0001-8607-9976](https://orcid.org/0000-0001-8607-9976)

Mikel F. Hurtado – Engineering School, Sustainable Research Center, Civil Engineering Department, Corporación Universitaria Minuto de Dios, Bogotá 11104, Colombia; Civil Engineering Department, UNIAGRARIA, Calle 170 Cra 53, Bogotá 110911, Colombia

Salvador Eslava – Department of Chemical Engineering and Centre for Processable Electronics, Imperial College London, South Kensington, London SW7 2AZ, United Kingdom; [ORCID.org/0000-0002-2416-3205](https://orcid.org/0000-0002-2416-3205)

Sixto Gimenez – Institute of Advanced Materials (INAM), Universitat Jaume I, Avenida de Vicent Sos Baynat, s/n, Castellón de la Plana 12006, Spain; [ORCID.org/0000-0002-4522-3174](https://orcid.org/0000-0002-4522-3174)

Kyoung-Shin Choi – Department of Chemistry, University of Wisconsin-Madison, Madison, Wisconsin 53706, United States; [ORCID.org/0000-0003-1945-8794](https://orcid.org/0000-0003-1945-8794)

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acscatal.6c01573>

■ ACKNOWLEDGMENTS

We thank the EU for financial support through the A-Leaf (732840) and SUN2CHEM (884444) projects. L.F. thanks the EU for a Marie Curie fellowship (658270) and the RyC fellowship (RYC2018-025394-I Fellowship), PID project (PID2021-128197NA-I00 and PID2024-160034NB-I00) and

CNS (CNS2023-144786) funded by MCIN/ AEI/10.13039/501100011033/FEDER, UE. S.E. and M.R. thank the EPSRC grant EP/S030727/1, and J.R.D. thanks EPSRC grant EP/Y026098/1 for financial support. A.K. thanks the EPSRC for a Capital Award Emphasising Support for Early Career Researchers and the Royal Society for an Equipment grant (RSG\R1\180434). L.S. thanks EPSRC grant EP/Z000343/1. S.G. thanks support from the project PID2023-152771OB-I00, funded by MCIN/ AEI/10.13039/501100011033/ and by "ERDF A way of making Europe", by the "European Union". C.A.M. and M.F.H. acknowledge the Research Cluster on Converging Sciences and Technologies (NBIC), Universidad Central for assisting the AFM measurements. K.-S.C. thanks the National Science Foundation (NSF) for financial support under grant no. CHE-2350199.

Author Contributions

S.S. contributed to conceptualization, investigation, and data curation. Y.W., V.L., L.S., Y.M., M.R., D.L., and M.F.H. contributed to investigation. C.A.M. contributed to conceptualization, investigation, formal analysis, and writing. A.K., S.E., K.-S.C., and S.G. contributed to investigation and resources. L.F. and J.R.D. contributed to conceptualization, funding acquisition, resources, supervision, and writing. All authors contributed to writing – review & editing.

Notes

The authors declare no competing financial interest.

REFERENCES

- (1) Berardi, S.; Drouet, S.; Francàs, L.; Gimbert-Suriñach, C.; Guttentag, M.; Richmond, C.; Stoll, T.; Llobet, A. Molecular Artificial Photosynthesis. *Chem. Soc. Rev.* **2014**, *43* (22), 7501–7519.
- (2) Lewis, N. S.; Nocera, D. G. Powering the Planet: Chemical Challenges in Solar Energy Utilization. *Proc. Natl. Acad. Sci. U. S. A.* **2006**, *103* (43), 15729–15735.
- (3) Galan-Mascaros, J. R. Photoelectrochemical Solar Fuels from Carbon Dioxide, Water and Sunlight. *Catal. Sci. Technol.* **2020**, *10* (7), 1967–1974.
- (4) Kafizas, A.; Godin, R.; Durrant, J. R. Charge Carrier Dynamics in Metal Oxide Photoelectrodes for Water Oxidation. *Semicond. Semimetals* **2017**, *97*, 3–46.
- (5) Chen, S.; Thind, S. S.; Chen, A. Nanostructured Materials for Water Splitting - State of the Art and Future Needs: A Mini-Review. *Electrochem. Commun.* **2016**, *63*, 10–17.
- (6) Lin, C.-Y.; Lai, Y.-H.; Mersch, D.; Reisner, E. $\text{Cu}_2\text{O}/\text{NiO}_x$ Nanocomposite as an Inexpensive Photocathode in Photoelectrochemical Water Splitting. *Chem. Sci.* **2012**, *3* (12), 3482–3487.
- (7) Zhang, J.; Cui, J.; Eslava, S. Oxygen Evolution Catalysts at Transition Metal Oxide Photoanodes: Their Differing Roles for Solar Water Splitting. *Adv. Energy Mater.* **2021**, *11* (13), No. 2003111.
- (8) Jian, J.-X.; Jokubavicius, V.; Syväjärvi, M.; Yakimova, R.; Sun, J. Nanoporous Cubic Silicon Carbide Photoanodes for Enhanced Solar Water Splitting. *ACS Nano* **2021**, *15* (3), 5502–5512.
- (9) Corby, S.; Francàs, L.; Selim, S.; Sachs, M.; Blackman, C.; Kafizas, A.; Durrant, J. R. Water Oxidation and Electron Extraction Kinetics in Nanostructured Tungsten Trioxide Photoanodes. *J. Am. Chem. Soc.* **2018**, *140* (47), 16168–16177.
- (10) Corby, S.; Rao, R. R.; Steier, L.; Durrant, J. R. The Kinetics of Metal Oxide Photoanodes from Charge Generation to Catalysis. *Nat. Rev. Mater.* **2021**, *6*, 1136–1155.
- (11) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Electrochemical and Photoelectrochemical Investigation of Water Oxidation with Hematite Electrodes. *Energy Environ. Sci.* **2012**, *5*, 7626–7636.
- (12) Tilley, S. D.; Cornuz, M.; Sivula, K.; Grätzel, M. Light-Induced Water Splitting with Hematite: Improved Nanostructure and Iridium Oxide Catalysis. *Angew. Chem., Int. Ed.* **2010**, *49* (36), 6405–6408.
- (13) Sudhagar, P.; Devadoss, A.; Nakata, K.; Terashima, C.; Fujishima, A. Enhanced Photoelectrocatalytic Water Splitting at Hierarchical $\text{Gd}^{3+}:\text{TiO}_2$ Nanostructures through Amplifying Light Reception and Surface States Passivation. *J. Electrochem. Soc.* **2015**, *162*, H108–H114.
- (14) Pesci, F. M.; Wang, G.; Klug, D. R.; Li, Y.; Cowan, A. J. Efficient Suppression of Electron–Hole Recombination in Oxygen-Deficient Hydrogen-Treated TiO_2 Nanowires for Photoelectrochemical Water Splitting. *J. Phys. Chem. C* **2013**, *117* (48), 25837–25844.
- (15) Nomellini, C.; Polo, A.; Mesa, C. A.; Pastor, E.; Marra, G.; Grigioni, I.; Dozzi, M. V.; Giménez, S.; Selli, E. Improved Photoelectrochemical Performance of $\text{WO}_3/\text{BiVO}_4$ Heterojunction Photoanodes via WO_3 Nanostructuring. *ACS Appl. Mater. Interfaces* **2023**, *15*, 52436–52447.
- (16) Liu, M.; De Leon Snapp, N.; Park, H. Water Photolysis with a Cross-Linked Titanium Dioxide Nanowire Anode. *Chem. Sci.* **2010**, *2* (1), 80–87.
- (17) Lee, S. Y.; Kim, J.; Vasquez, R.; Ng, E.; Lee, H. J.; Mora-Seró, I.; Giménez, S. Comparative Study of Bulk and Nanoscale BiVO_4 Photoanodes in Photoelectrochemical Oxidation Reactions. *Adv. Mater. Interfaces* **2025**, *12* (19), No. e00543.
- (18) Zhang, H.; Li, H.; Wang, Z.; Zheng, Z.; Wang, P.; Liu, Y.; Zhang, X.; Qin, X.; Dai, Y.; Huang, B. Fabrication of BiVO_4 Photoanode Consisted of Mesoporous Nanoparticles with Improved Bulk Charge Separation Efficiency. *Appl. Catal., B* **2018**, *238*, 586–591.
- (19) Hegner, F. S.; Herraiz-Cardona, I.; Cardenas-Morcoso, D.; López, N.; Galán-Mascarós, J. R.; Gimenez, S. Cobalt Hexacyanoferrate on BiVO_4 Photoanodes for Robust Water Splitting. *ACS Appl. Mater. Interfaces* **2017**, *9* (43), 37671–37681.
- (20) Kim, T. W.; Choi, K.-S. Nanoporous BiVO_4 Photoanodes with Dual-Layer Oxygen Evolution Catalysts for Solar Water Splitting. *Science* **2014**, *343* (6174), 990–994.
- (21) Cowan, A. J.; Tang, J.; Leng, W.; Durrant, J. R.; Klug, D. R. Water Splitting by Nanocrystalline TiO_2 in a Complete Photoelectrochemical Cell Exhibits Efficiencies Limited by Charge Recombination. *J. Phys. Chem. C* **2010**, *114* (9), 4208–4214.
- (22) Mesa, C. A.; Kafizas, A.; Francàs, L.; Pendlebury, S. R.; Pastor, E.; Ma, Y.; Le Formal, F.; Mayer, M. T.; Grätzel, M.; Durrant, J. R. Kinetics of Photoelectrochemical Oxidation of Methanol on Hematite Photoanodes. *J. Am. Chem. Soc.* **2017**, *139*, 11537–11543.
- (23) McCrory, C. C. L.; Jung, S.; Ferrer, I. M.; Chatman, S. M.; Peters, J. C.; Jaramillo, T. F. Benchmarking Hydrogen Evolving Reaction and Oxygen Evolving Reaction Electrocatalysts for Solar Water Splitting Devices. *J. Am. Chem. Soc.* **2015**, *137* (13), 4347–4357.
- (24) Safshekan, S.; Herraiz-Cardona, I.; Cardenas-Morcoso, D.; Ojani, R.; Haro, M.; Gimenez, S. Solar Energy Storage by a Heterostructured $\text{BiVO}_4\text{--PbO}_x$ Photocapacitive Device. *ACS Energy Lett.* **2017**, *2* (2), 469–475.
- (25) Sebastián-Pascual, P.; Escudero-Escribano, M. Surface Characterization of Copper Electrocatalysts by Lead Underpotential Deposition. *J. Electroanal. Chem.* **2021**, *896*, No. 115446.
- (26) Moss, B.; Babacan, O.; Kafizas, A.; Hankin, A. A Review of Inorganic Photoelectrode Developments and Reactor Scale-Up Challenges for Solar Hydrogen Production. *Adv. Energy Mater.* **2021**, *11* (13), No. 2003286.
- (27) Bjarke, J.; Mygind, V.; Rost, M. J.; Escudero-Escribano, M. The Hidden Complexities of Electrochemically Active Surface Area Measurements. *ACS Energy Lett.* **2026**, *11* (3), 2508–2520.
- (28) Li, J.; Chen, H.; Triana, C. A.; Patzke, G. R. Hematite Photoanodes for Water Oxidation: Electronic Transitions, Carrier Dynamics, and Surface Energetics. *Angew. Chem., Int. Ed.* **2021**, *60* (34), 18380–18396.
- (29) Barroso, M.; Pendlebury, S. R.; Cowan, A. J.; Durrant, J. R. Charge Carrier Trapping, Recombination and Transfer in Hematite

- ([Small Alpha]-Fe₂O₃) Water Splitting Photoanodes. *Chem. Sci.* **2013**, 4 (7), 2724–2734.
- (30) Barroso, M.; Mesa, C. A.; Pendlebury, S. R.; Cowan, A. J.; Hisatomi, T.; Sivula, K.; Grätzel, M.; Klug, D. R.; Durrant, J. R. Dynamics of Photogenerated Holes in Surface Modified α -Fe₂O₃ Photoanodes for Solar Water Splitting. *Proc. Natl. Acad. Sci.* **2012**, 109 (39), 15640–15645.
- (31) Zhang, Z.; Nagashima, H.; Tachikawa, T. Ultra-Narrow Depletion Layers in a Hematite Mesocrystal-Based Photoanode for Boosting Multihole Water Oxidation. *Angew. Chem.* **2020**, 132 (23), 9047–9054.
- (32) Selim, S.; Pastor, E.; García-Tecedor, M.; Morris, M. R.; Francà, L.; Sachs, M.; Moss, B.; Corby, S.; Mesa, C. A.; Gimenez, S.; Kafizas, A.; Bakulin, A. A.; Durrant, J. R. Impact of Oxygen Vacancy Occupancy on Charge Carrier Dynamics in BiVO₄ Photoanodes. *J. Am. Chem. Soc.* **2019**, 141, 18791–18798.
- (33) Mesa, C. A.; Pastor, E.; Francà, L. UV–Vis Operando Spectroelectrochemistry for (Photo)Electrocatalysis: Principles and Guidelines. *Curr. Opin. Electrochem.* **2022**, 35, No. 101098.
- (34) Chen, R.; Zhang, D.; Wang, Z.; Li, D.; Zhang, L.; Wang, X.; Fan, F.; Li, C. Linking the Photoinduced Surface Potential Difference to Interfacial Charge Transfer in Photoelectrocatalytic Water Oxidation. *J. Am. Chem. Soc.* **2023**, 145 (8), 4667–4674.
- (35) Francàs, L.; Mesa, C. A.; Pastor, E.; Le Formal, F.; Durrant, J. R. Rate Law Analysis of Water Splitting Photoelectrodes. In *Advances in Photoelectrochemical Water Splitting: Theory, Experiment and Systems Analysis*, Tilley, S. D., Lany, S., van de Krol, R., Eds.; The Royal Society of Chemistry, **2018**.
- (36) Le Formal, F.; Pastor, E.; Tilley, S. D.; Mesa, C. A.; Pendlebury, S. R.; Grätzel, M.; Durrant, J. R. Rate Law Analysis of Water Oxidation on a Hematite Surface. *J. Am. Chem. Soc.* **2015**, 137 (20), 6629–6637.
- (37) Ma, Y.; Mesa, C. A.; Pastor, E.; Kafizas, A.; Francàs, L.; Le Formal, F.; Pendlebury, S. R.; Durrant, J. R. Rate Law Analysis of Water Oxidation and Hole Scavenging on a BiVO₄ Photoanode. *ACS Energy Lett.* **2016**, No. 1, 618–623.
- (38) Boettcher, S. W.; Surendranath, Y. Heterogeneous Electrocatalysis Goes Chemical. *Nat. Catal.* **2021**, 4, 4–5.
- (39) Govindarajan, N.; Chu, A. T.; Hahn, C.; Surendranath, Y. The Overlooked Role of Adsorption Isotherms in Electrocatalysis. *Nat. Catal.* **2025**, 8 (12), 1254–1259.
- (40) Gaje, A.; Rao, R.; Mesa, C. A.; Keller, N.; Francàs, L.; Durrant, J. R.; Pastor, E. Molecular-Scale Interactions in Heterogeneous (Photo)Electrocatalysis. *Nat. Catal.* **2026**, 9 (3), 248–256.
- (41) Righi, G.; Plescher, J.; Schmidt, F. P.; Campen, R. K.; Fabris, S.; Knop-Gericke, A.; Schlögl, R.; Jones, T. E.; Teschner, D.; Piccinin, S. On the Origin of Multihole Oxygen Evolution in Haematite Photoanodes. *Nat. Catal.* **2022**, 5 (10), 888–899.
- (42) Li, J.; Wan, W.; Triana, C. A.; Chen, H.; Zhao, Y.; Mavrokefalos, C. K.; Patzke, G. R. Reaction Kinetics and Interplay of Two Different Surface States on Hematite Photoanodes for Water Oxidation. *Nat. Commun.* **2021**, 12 (1), 1–9.
- (43) Kafizas, A.; Ma, Y.; Pastor, E.; Pendlebury, S. R.; Mesa, C.; Francà, L.; Le Formal, F.; Noor, N.; Ling, M.; Sotelo-Vazquez, C.; Carmalt, C. J.; Parkin, I. P.; Durrant, J. R. Water Oxidation Kinetics of Accumulated Holes on the Surface of a TiO₂ Photoanode: A Rate Law Analysis. *ACS Catal.* **2017**, 7 (7), 4896–4903.
- (44) Pastor, E.; Le Formal, F.; Mayer, M. T.; Tilley, S. D.; Francàs, L.; Mesa, C. A.; Grätzel, M.; Durrant, J. R. Spectroelectrochemical Analysis of the Mechanism of (Photo)Electrochemical Hydrogen Evolution at a Catalytic Interface. *Nat. Commun.* **2017**, 8, No. 14280.
- (45) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Hamann, T.; Bisquert, J. Water Oxidation at Hematite Photoelectrodes: The Role of Surface States. *J. Am. Chem. Soc.* **2012**, 134 (9), 4294–4302.
- (46) Mesa, C. A.; Steier, L.; Moss, B.; Francàs, L.; Thorne, J. E.; Grätzel, M.; Durrant, J. R. Impact of the Synthesis Route on the Water Oxidation Kinetics of Hematite Photoanodes. *J. Phys. Chem. Lett.* **2020**, 11, 7285–7290.
- (47) Sachs, M.; Pastor, E.; Kafizas, A.; Durrant, J. R. Evaluation of Surface State Mediated Charge Recombination in Anatase and Rutile TiO₂. *J. Phys. Chem. Lett.* **2016**, 7, 3742–3746.
- (48) Xiao-e, L.; Green, A. N. M.; Haque, S. A.; Mills, A.; Durrant, J. R. Light-Driven Oxygen Scavenging by Titania/Polymer Nanocomposite Films. *J. Photochem. Photobiol., A* **2004**, 162 (2–3), 253–259.
- (49) Regue, M.; Sibby, S.; Ahmet, I. Y.; Friedrich, D.; Abdi, F. F.; Johnson, A. L.; Eslava, S. TiO₂ Photoanodes with Exposed {0 1 0} Facets Grown by Aerosol-Assisted Chemical Vapor Deposition of a Titanium Oxo/Alkoxy Cluster†. *J. Mater. Chem. A Mater.* **2019**, 7, 19161–19172.
- (50) Kay, A.; Cesar, I.; Grätzel, M. New Benchmark for Water Photooxidation by Nanostructured α -Fe₂O₃ Films. *J. Am. Chem. Soc.* **2006**, 128 (49), 15714–15721.
- (51) Cornuz, M.; Grätzel, M.; Sivula, K. Preferential Orientation in Hematite Films for Solar Hydrogen Production via Water Splitting. *Chem. Vap. Deposition* **2010**, 16 (10–12), 291–295.
- (52) Steier, L.; Luo, J.; Schreier, M.; Mayer, M. T.; Sajavaara, T.; Grätzel, M. Low-Temperature Atomic Layer Deposition of Crystalline and Photoactive Ultrathin Hematite Films for Solar Water Splitting. *ACS Nano* **2015**, 9 (12), 11775–11783.
- (53) Ma, Y.; Pendlebury, S. R.; Reynal, A.; Le Formal, F.; Durrant, J. R. Dynamics of Photogenerated Holes in Undoped BiVO₄ Photoanodes for Solar Water Oxidation. *Chem. Sci.* **2014**, 5 (8), 2964–2973.
- (54) Wang, X.; Kafizas, A.; Li, X.; Moniz, S. J. A.; Reardon, P. J. T.; Tang, J.; Parkin, I. P.; Durrant, J. R. Transient Absorption Spectroscopy of Anatase and Rutile: The Impact of Morphology and Phase on Photocatalytic Activity. *J. Phys. Chem. C* **2015**, 119 (19), 10439–10447.
- (55) Francàs, L.; Selim, S.; Corby, S.; Lee, D.; Mesa, C. A.; Pastor, E.; Choi, K.-S.; Durrant, J. R. Water Oxidation Kinetics of Nanoporous BiVO₄ Photoanodes Functionalised with Nickel/Iron Oxyhydroxide Electrocatalysts. *Chem. Sci.* **2021**, 12 (21), 7442–7452.
- (56) O’rourke, C.; Mills, A.; Li, R. Probing P₂₅ TiO₂ Photocatalysis Using Photoinduced Absorption Spectroscopy (PIAS). *Chem. Commun.* **2021**, 57 (10), 1242–1245.
- (57) Zhang, Y.; Zhang, H.; Liu, A.; Chen, C.; Song, W.; Zhao, J. Rate-Limiting O–O Bond Formation Pathways for Water Oxidation on Hematite Photoanode. *J. Am. Chem. Soc.* **2018**, 140 (9), 3264–3269.
- (58) Yuan, J.; Yuan, Y.; Zhang, J.; Xu, H.; Mao, Z.; Ma, Y. Mechanistic Insights into Selective Acetaldehyde Formation from Ethanol Oxidation on Hematite Photoanodes by Operando Spectroelectrochemistry. *ChemSusChem* **2022**, 15 (5), No. e202102313.
- (59) Mesa, C. A.; Francàs, L.; Yang, K. R.; Garrido-Barros, P.; Pastor, E.; Ma, Y.; Kafizas, A.; Rosser, T. E.; Mayer, M. T.; Reisner, E.; Grätzel, M.; Batista, V. S.; Durrant, J. R. Multihole Water Oxidation Catalysis on Haematite Photoanodes Revealed by Operando Spectroelectrochemistry and DFT. *Nat. Chem.* **2020**, 12, 82–89.
- (60) He, T.; Benetti, D.; Tseng, C.; Moss, B.; Teschner, D.; Jones, T. E.; Kafizas, A.; Grätzel, M.; Piccinin, S.; Durrant, J. R. Observation of Transition from Rate Law to Butler–Volmer Controlled Water Oxidation Kinetics on Hematite Photoanodes. *J. Am. Chem. Soc.* **2026**, 148 (5), 4833–4838.
- (61) Warren, S. C.; Voitchovsky, K.; Dotan, H.; Leroy, C. M.; Cornuz, M.; Stellacci, F.; Hébert, C.; Rothschild, A.; Grätzel, M. Identifying Champion Nanostructures for Solar Water-Splitting. *Nat. Mater.* **2013**, 12 (9), 842–849.
- (62) Morales, D. M.; Risch, M. Seven Steps to Reliable Cyclic Voltammetry Measurements for the Determination of Double Layer Capacitance. *J. Phys.: Energy* **2021**, 29 (46), No. 465705.
- (63) Pastor, E.; Montañés, L.; Gutiérrez-Blanco, A.; Hegner, F. S.; Mesa, C. A.; López, N.; Giménez, S. The Role of Crystal Facets and Disorder on Photo-Electrosynthesis. *Nanoscale* **2022**, 14 (42), 15596–15606.
- (64) Grave, D. A.; Klotz, D.; Kay, A.; Dotan, H.; Gupta, B.; Visoly-Fisher, I.; Rothschild, A. Effect of Orientation on Bulk and Surface Properties of Sn-Doped Hematite (α -Fe₂O₃) Heteroepitaxial Thin Film Photoanodes. *J. Phys. Chem. C* **2016**, 120 (S1), 28961–28970.
- (65) Yatom, N.; Gollapalli, P.; Grave, D. A.; Rothschild, A.; Casparly Toroker, M. Understanding Surface Charging Limitations

of Hematite Photoanodes through Combining Cathodic Discharge Measurements and Computational Modeling. *J. Catal.* **2026**, *456*, No. 116751.

(66) Kafizas, A.; Francà, L.; Sotelo-Vazquez, C.; Ling, M.; Li, Y.; Glover, E.; Mc Cafferty, L.; Blackman, C.; Darr, J.; Parkin, I. Optimizing the Activity of Nanoneedle Structured WO_3 Photoanodes for Solar Water Splitting: Direct Synthesis via Chemical Vapor Deposition. *J. Phys. Chem. C* **2017**, *121*, 5983–5993.

(67) Cowan, A. J.; Leng, W.; Barnes, P. R. F.; Klug, D. R.; Durrant, J. R. Charge Carrier Separation in Nanostructured TiO_2 Photoelectrodes for Water Splitting. *Phys. Chem. Chem. Phys.* **2013**, *15* (22), 8772.

(68) Cowan, A. J.; Durrant, J. R. Long-Lived Charge Separated States in Nanostructured Semiconductor Photoelectrodes for the Production of Solar Fuels. *Chem. Soc. Rev.* **2013**, *42* (6), 2281–2293.

(69) Le Formal, F.; Pendlebury, S. R.; Cornuz, M.; Tilley, S. D.; Grätzel, M.; Durrant, J. R. Back Electron–Hole Recombination in Hematite Photoanodes for Water Splitting. *J. Am. Chem. Soc.* **2014**, *136* (6), 2564–2574.

(70) Ma, Y.; Le Formal, F.; Kafizas, A.; Pendlebury, S. R.; Durrant, J. R. Efficient Suppression of Back Electron/Hole Recombination in Cobalt Phosphate Surface-Modified Undoped Bismuth Vanadate Photoanodes. *J. Mater. Chem. A* **2015**, *3*, 20649–20657.

(71) Klahr, B.; Gimenez, S.; Fabregat-Santiago, F.; Bisquert, J.; Hamann, T. W. Photoelectrochemical and Impedance Spectroscopic Investigation of Water Oxidation with “Co–Pi”-Coated Hematite Electrodes. *J. Am. Chem. Soc.* **2012**, *134*, 16693–16700.

(72) Wang, S.; Liu, G.; Wang, L. Crystal Facet Engineering of Photoelectrodes for Photoelectrochemical Water Splitting. *Chem. Rev.* **2019**, *119* (8), 5192–5247.

(73) Wang, S.; Chen, H.; Gao, G.; Butburee, T.; Lyu, M.; Thaweesak, S.; Yun, J. H.; Du, A.; Liu, G.; Wang, L. Synergistic Crystal Facet Engineering and Structural Control of WO_3 Films Exhibiting Unprecedented Photoelectrochemical Performance. *Nano Energy* **2016**, *24*, 94–102.

(74) Luo, H.; Barrio, J.; Sunny, N.; Li, A.; Steier, L.; Shah, N.; Stephens, I. E. L.; Titirici, M.-M. Progress and Perspectives in Photo- and Electrochemical-Oxidation of Biomass for Sustainable Chemicals and Hydrogen Production. *Adv. Energy Mater.* **2021**, *11* (43), No. 2101180.

(75) Ng, E.; Mesa, C. A.; Más-Marzá, E.; Giménez, S. Current-Dependent Product Distribution and Reaction Mechanisms of Glycerol Electrooxidation on Nickel. *ChemElectroChem* **2025**, *12* (3), No. e202400534.

(76) Liu, D.; Liu, J. C.; Cai, W.; Ma, J.; Yang, H. Bin; Xiao, H.; Li, J.; Xiong, Y.; Huang, Y.; Liu, B. Selective Photoelectrochemical Oxidation of Glycerol to High Value-Added Dihydroxyacetone. *Nat. Commun.* **2019**, *10* (1), No. 1779.

(77) Zachäus, C.; Abdi, F. F.; Peter, L. M.; Van De Krol, R. Photocurrent of BiVO_4 Is Limited by Surface Recombination, Not Surface Catalysis. *Chem. Sci.* **2017**, *8*, 3712.

(78) Klahr, B.; Gimenez, S.; Zandi, O.; Fabregat-Santiago, F.; Hamann, T. Competitive Photoelectrochemical Methanol and Water Oxidation with Hematite Electrodes. *ACS Appl. Mater. Interfaces* **2015**, *7* (14), 7653–7660.

(79) Peter, L. M.; Upul Wijayantha, K. G.; Tahir, A. A. Kinetics of Light-Driven Oxygen Evolution at $\alpha\text{-Fe}_2\text{O}_3$ Electrodes. *Faraday Discuss.* **2012**, *155*, 309–322.

(80) Gärtner, W. W. Depletion-Layer Photoeffects in Semiconductors. *Phys. Rev.* **1959**, *116* (1), 84–87.

(81) Gerischer, H. The Impact of Semiconductors On The Concepts Of Electrochemistry. *Electrochim. Acta* **1990**, *35* (11), 1677–1699.

(82) Sodergren, S.; Hagfeldt, A.; Olsson, J.; Lindquist, S. E. Theoretical Models for the Action Spectrum and the Current-Voltage Characteristics of Microporous Semiconductor Films in Photoelectrochemical Cells. *J. Phys. Chem. C* **1994**, *98* (21), 5552–5556.

(83) Moss, B.; Hegner, F. S.; Corby, S.; Selim, S.; Francà, L.; López, N.; Giménez, S.; Galán-Mascarós, J.-R.; Durrant, J. R. Unraveling

Charge Transfer in CoFe Prussian Blue Modified BiVO_4 Photoanodes. *ACS Energy Lett.* **2018**, 337–342.

(84) Albery, W. J.; Bartlett, P. N. The Transport and Kinetics of Photogenerated Carriers in Colloidal Semiconductor Electrode Particles. *J. Electrochem. Soc.* **1984**, *131* (2), 315–325.

(85) Curran, J. S.; Lamouche, D. Transport and Kinetics in Photoelectrolysis by Semiconductor Particles in Suspension. *J. Phys. Chem. C* **1983**, *87* (26), 5405–5411.

(86) Cesar, I.; Sivula, K.; Kay, A.; Zboril, R.; Grätzel, M. Influence of Feature Size, Film Thickness, and Silicon Doping on the Performance of Nanostructured Hematite Photoanodes for Solar Water Splitting. *J. Phys. Chem. C* **2009**, *113*, 772–782.

(87) Liu, Y.; Le Formal, F.; Boudoire, F.; Guijarro, N. N. Hematite Photoanodes for Solar Water Splitting: A Detailed Spectroelectrochemical Analysis on the PH-Dependent Performance. *ACS Appl. Energy Mater.* **2019**, *2* (9), 6825–6833.