Multicomposite Nanostructured Hematite–Titania Photoanodes with Improved Oxygen Evolution: The Role of the Oxygen Evolution Catalyst

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Supporting Information

ABSTRACT: We present a sol–gel processed hematite–titania-based photoanode, which exhibits a photocurrent of up to 2.5 mA/cm² at 1.23 V_RHE under simulated AM 1.5 G illumination (100 mW/cm²) thanks to the addition of an amorphous cocatalyst with the nominal composition Fe_{20}Cr_{40}Ni_{40}O_{x}. To unveil the role of the cocatalyst interconnected to the photoanode, we performed impedance measurements. According to the one order of magnitude higher value for the capacitance associated with surface states (C_SS) compared to the bare photoanode, the function of the catalyst–photoanode interface resembles that of a p–n-like junction. In addition, the charge transfer resistance associated with charge transfer processes from surface states (R_CT) was unchanged at potentials between 0.8 and 1.1 V_RHE after adding the cocatalyst, indicating that the catalyst has a negligible effect on the hole transport to the electrolyte. The understanding of the role of oxygen evolution catalysts (OECs) in conjunction with the photoanodes is particularly important for water splitting because most OECs are studied separately at considerably higher potentials compared to the potentials at which photoanode materials are operated.

INTRODUCTION

The urge to replace fossil fuels by a renewable energy source will be predominant in this century to limit global warming. Although solar cells exhibit excellent quantum efficiencies, losses occur when electric power is stored in batteries to bypass peaks with high power generation. With direct photoelectrochemical water splitting, one has the clear advantage to transform sunlight directly into hydrogen, which has a high energy density per unit weight. Compared to those of TiO_2 and WO_3, hematite photoanodes exhibit a high theoretically achievable solar-to-hydrogen efficiency (15.5%) coinciding with its narrow band gap of ca. 2.1 eV. However, inherent drawbacks such as poor e⁻ and h⁺ conductivity, low charge carrier mobility and lifetime, large visible light absorption depth, and slow water oxidation kinetics limit its performance. These shortcomings, which lead to increased charge carrier recombination, have been addressed by nanostructuring, by constructing hierarchical assemblies, by doping (e.g., with Sn, Si, Mo, Cr, Pt, and Ti), and through the introduction of under- and overlayers at the back contact and on top of the photoanodes, respectively.

Carrier recombination, have been addressed by nanostructuring, by constructing hierarchical assemblies, by doping (e.g., with Sn, Si, Mo, Cr, Pt, and Ti), and through the introduction of under- and overlayers at the back contact and on top of the photoanodes, respectively. Moreover, such ultrathin (1–2 nm) overlayers enable n/p-type doping at the interfaces. The role of Nb_2O_5 underlayers is attributed to a "hole-mirror" effect and hence inhibits recombination. Improvements in conductivity thanks to differently aligned valence and conduction bands in heterojunction engineered photoanodes. Such a system was reported for Fe_2O_3–Fe_2TiO_5. Another reason might be that hematite is completely transformed into another phase, for example, through high-temperature annealing, as described for a WO_3–Fe_2WO_6 photoanode. Charge transport was further reported to be promoted by the introduction of thin layers at the hematite–F:SnO_2 contact. In this case, the beneficial effects depend on the type of the layer. Whereas a SiO_2 coating indirectly leads to improved morphology by acting as a seeding layer for the subsequently deposited hematite layer, the role of Nb_2O_5 underlayers is attributed to a "hole-mirror" effect and hence inhibits recombination. Moreover, such ultrathin (1–2 nm) underlayers enable n/p-type doping at the interfaces upon annealing, comparable to Sn doping at the hematite–F:SnO_2 interface detected after high-temperature treatments, thus improving charge transfer.

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regarding hematite-based photoanodes were also achieved by “disorder engineering” upon annealing under reducing conditions. The photocurrent enhancement through hydrogen (plasma) reduction is highly dependent on the process parameters and intends to avoid the formation of Fe₂O₄ responsible for dramatic performance lowering.³⁴ Wet chemical reduction with “H” sources also leads to a pronounced improvement of the performance, which is attributed to surface engineering of the hematite photoanode, underlining the importance to differentiate between beneficial surface and adverse bulk effects of reduced α-Fe₂O₃ containing Fe²⁺ impurities.³⁵

Generally, hematite-based photoanodes show a rather high onset potential, attributed to intrinsic surface states, which pin the Fermi level and cause a fixed barrier height. Consequently, the degree of band bending, which in turn is positively correlated with e⁻/h⁺ separation, is dictated by the density and energy distribution of surface states.³⁶,³⁷ Attempts to reduce the negative impacts of surface states and thus to lower the flat band potential (E₆₈) include high-temperature annealing,³⁸ long annealing times,³⁸ or surface modifications with fluorides³⁹ or zinc ions.⁴⁰ Moreover, passivation of surface states was realized with ultrathin coatings of Al₂O₃ and Ga₂O₃.¹⁸

Oxygen evolution catalysts (OECs) in turn facilitate hole transfer to the electrolyte, whereas both effects, passivation of surface states and acceleration of hole transfer, lead to a cathodic shift in the onset potential.¹⁷ The activity of a cocatalyst depends also on the photoanode itself, that is, the Eᵛᵣₑₚ potential (Eᵛᵣₑₚ) and the resulting adsorption energies of reduced e⁻/h⁺ at the semiconductor/electrolyte interface, which is dependent on the band structure of the semiconductor.¹⁷,¹⁸

In this contribution, we present a hematite–titania photoanode covered with a catalyst fabricated by a simple spin-coating process. The hematite–titania composite layer was prepared by liquid phase processing using preformed nanoparticles with defined size, crystallinity, and shape. The improved activity compared to that of bare hematite stems from the incorporation of Ti, resulting in the formation of a Fe₂O₃–Fe₂O₃ heterojunction.⁶⁴ The photoanode is further modified with an amorphous ternary Fe–Ni-based cocatalyst⁶⁵,⁶⁶ with nominal composition “Fe₃₀Ni₃⁰Cr₄₀Oₓ”, which was previously shown by Gerken et al.⁶⁷ to be a promising material with respect to oxygen evolution characteristics. Most studies on OECs are conducted in the dark in the oxygen evolution potential range. However, we wanted to gain further insights into the interplay between photoanodes and catalysts; therefore, we studied our system at potentials (e.g., 0.8–1.1 V_RHE) at which photoanode materials are usually operated. Impedance spectroscopy measurements revealed that the reason for the drastic improvement of the performance upon adding the photocatalyst layer on top of the photoanode does not stem from accelerated hole transfer to the electrolyte but is due to the formation of a p/n-type junction at the photoanode–catalyst interface.

■ RESULTS AND DISCUSSION

Voltammetric and Efficiency Measurements. The performance of the hematite–titania photoanodes could be drastically improved after the addition of the overlayer with nominal composition “Fe₃₀Cr₄₀Ni₃⁰Oₓ”, as depicted by voltammetric measurements in Figure 1.

![Figure 1. Photocurrent density of a Fe₂O₃–TiO₂ photoanode before and after the addition of an amorphous overlayer with nominal composition “Fe₃₀Cr₄₀Ni₃⁰Oₓ” measured in 1 M NaOH under simulated AM 1.5 G illumination (100 mW/cm²).](image-url)
pronounced in the visible range and accounts for about 10% improvement between 400 and 500 nm, whereas at longer wavelengths, the enhancement is negligible. In addition, the catalyst layer shows no parasitic light absorption, which enables nearly full light penetration of the photoanode (Figure S5, SI).

The chopped light scan (Figure 3) reveals that the cathodic photocurrent decay is much higher for "over-Fe₂O₃-TiO₂" as compared to that for the bare photoanode at low potentials, whereas the trend reverses between 1.0 and 1.2 V_RHE. The cathodic photocurrent decays are of about the same magnitude in "bare-Fe₂O₃-TiO₂" over the entire voltage range. The cathodic transient photocurrent decay can be ascribed to three different recombination pathways: (i) accumulation of holes near the surface, (ii) accumulation of electrons in the bulk, or (iii) trapping of e⁻ or h⁺ at surface states. Backside illumination of the bare photoanode showed that the photocurrent is nearly identical or even slightly lower (Figure S1, SI). Therefore, accumulation of electrons in the bulk can be ruled out. In the work of Du et al.⁶⁹ and Jang et al.,⁷⁰ the open circuit potentials in the dark are anodically shifted after depositing the NiFeOₓ overlayer. The cathodic shift under illumination was understood to result from a greater photovoltage generation; thus, the increase in photocurrent was attributed to improved thermodynamics, rather than improved oxygen evolution kinetics. Moreover, the photocurrent enhancement throughout the entire potential range could point toward improved thermodynamic processes.

**Impedance Measurements.** To unveil the role of the overlayer regarding charge transfer processes and capacitances, we performed impedance measurements (Figure 4). Because the surface of the photoanodes is sensitive to surface quality losses during impedance measurements, two similarly performing bare-Fe₂O₃-TiO₂ photoanodes were used and only one was overlayered. First, we performed Mott–Schottky analysis (in the dark) to determine E₀, and the donor density (N₀). The Nyquist plots (Figure S9, SI) were fitted to a Randles circuit, and the potential-dependent capacitances were plotted according to the Mott–Schottky equation

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 N_e \varepsilon A^2} \left( E - E_{fb} - \frac{kT}{\epsilon} \right)$$

where N₀ is the donor density (m⁻³), A is the electrode area (m²), ε is the elementary charge (1.60 × 10⁻¹⁹ C), E₀ is the flat band potential (V), ε is the vacuum permittivity (8.85 × 10⁻¹² F m⁻¹), εᵣ is the relative dielectric constant of hematite (εᵣ = 60), k is the Boltzmann constant (1.38 × 10⁻²³ J K⁻¹), and T is the absolute temperature (in K). The slope is inversely proportional to N₀, meaning that the larger the doping, the smaller the slope. The analysis of the slope for the bare-Fe₂O₃-TiO₂ photoanode shows that the donor density (N₀) is about 3.19 × 10¹⁸ cm⁻³, whereas a donor density of about 2.12 × 10¹⁸ cm⁻³ was measured for over-Fe₂O₃-TiO₂ (Table S1, SI). The slightly lower value obtained for the overlayered photoanode suggests that the donor density dropped. From the intersect of 1/C² at the x-axis, E₀, can be obtained (Figure S8, Table S1, SI). The values for over-Fe₂O₃-TiO₂ and bare-Fe₂O₃-TiO₂ are 0.68 and 0.66 V, respectively (Table S1, SI). The standard deviation suggests that these two photoanodes do not significantly differ, indicating that the enhanced performance is not due to a shift in the flat band potential. Assuming that charge transfer occurs predominantly via surface states and due to the fact that the contribution of the Helmholtz capacitance (C_H) can be neglected, because Nₐ is well below 10⁰⁵ cm⁻³, the circuit shown in Figure S10 (SI) was used and proved to be a good estimation for the surface state capacitance (Cₛₐₜ), the bulk capacitance (Cₑₑₓₐᵛ), the surface charge transfer resistance (Rₛₑₑₓₐᵛ), and the trapping resistance (Rᵥₑₑₓₐᵛ).
Impedance measurements of the illuminated samples were performed in the potential range between 0.8 and 1.1 V RHE. As expected, the bulk capacitance \( (C_{\text{bulk}}) \) is not significantly influenced by the addition of the overlayer (Figure S15, SI). The similar \( R_{\text{ct,ss}} \) value for both photoanodes (Figure 4) proposes that the charge transfer to the aqueous electrolyte is not improved by the overlayer. However, the \( C_{\text{ss}} \) value for over-\( \text{Fe}_2\text{O}_3-\text{TiO}_2 \) is substantially higher, namely, by approximately 1 order of magnitude compared to that for bare-\( \text{Fe}_2\text{O}_3-\text{TiO}_2 \). Furthermore, the peak of \( C_{\text{ss}} \) is consistent with the inflection potential in the photocurrent curve. If the "\( \text{Fe}_{20}\text{Cr}_{30}\text{Ni}_{40}\text{O}_{x} \)" layer acted as a true water oxidation catalyst, a lowering of \( C_{\text{ss}} \) would have been expected.\(^{43}\) Furthermore, \( C_{\text{ss}} \) is much higher over the entire potential range, which suggests that the photocurrent improvement stems mainly from the capability of the catalyst to store holes, representing a thermodynamic improvement.

NiFeO\(_x\)-hematite heterostructures are assumed to form a p/n-type junction, as stated by Zandi et al.,\(^{73}\) owing to the improved turn-on photovoltage as a result of the addition of the catalyst.\(^{70}\) Moreover, in our case, \( R_{\text{trapping}} \) is slightly lower after coating the photoanode. This supports the observation made by Du et al.,\(^{69}\) that FeNiO\(_x\)-type overlayers on hematite are able to reduce Fermi level pinning. A lower \( R_{\text{trapping}} \) value indicates that the catalyst thus extracts holes located in the traps created by surface states in the hematite–titania layer. Induced by the addition of titania, these traps are presumably located few hundred millivolts more negative than the valence band position of the hematite–titania composite.\(^{64}\)

**Microstructural and Composition Effects.** Impedance measurements performed by Morales-Guio et al.\(^{74}\) on samples with Fe/Ni = 70:30 revealed a \( C_{\text{ss}} \) and \( R_{\text{ct,ss}} \) value decrease upon photoelectrodeposition on hematite, pointing toward an acceleration of water oxidation kinetics. In our case, the Fe–Ni-type catalyst additionally contains chromium (Fe/Ni/Cr = 58:24:40, Table S4, SI), which is leaching out upon electrolysis at least from the outermost surface as confirmed by X-ray photoelectron spectroscopy (XPS) and secondary-ion mass spectrometry (SIMS) analyses (Figures S7, S13, and S14, SI), as expected when looking at Pourbaix diagrams.\(^{75}\) The removal of chromium from the top of the catalyst layer increases the surface roughness\(^{67}\) and may promote permeability of the
catalyst by the electrolyte, thereby reducing the potential drop at the catalyst–electrolyte interface. The loss of Cr and the change in intensity of the Ni 2p photopeaks (XPS) further suggest that the catalyst layer rearranges upon polarization (Figure S7, SI). In a study by Gerken et al., the composition Fe$_{20}$Ni$_{40}$Cr$_{40}$O$_x$ was among those with the highest roughness factors. Only earth alkaline metal-containing compositions outperformed the composition Fe$_{20}$Ni$_{40}$Cr$_{40}$O$_x$ in terms of roughness factor according to a screening of different catalysts. Compared to that in a dense catalyst, no potential drop across the Helmholtz layer is expected to occur because the electronic charge is compensated by the coupled ion motion in the electrolyte.

Oxygen evolution measurements (Figure S) were performed to study the effect of the catalyst on the Faradaic efficiency. The Faradaic efficiency is measured with respect to the photocurrent, which directly allows us to gain further insights into the ability of the catalyst to evolve oxygen. Indeed, the Faradaic efficiency rises by about 9%, pointing toward the ability of the catalyst to improve the oxygen evolution kinetics. Although the main improvement in photocurrent is linked to thermodynamic effects, as found by impedance spectroscopy, one has to keep in mind that the oxygen evolution was measured at a potential of 1.23 V RHE whereas the impedance analysis was performed at potentials between 0.8 and 1.1 V RHE. The more the anodic potential, the stronger the oxidative power of holes becomes. Thus, effects such as partial charge transfer activation in the “Ni–O–Fe” bond facilitates stabilization of redox shuttles, which are supposed to drive the water oxidation. Regarding the implementation of such a photoanode into a tandem cell, the observations made at low potential are important because the operating point for tandem cells, depending on the band gap and band position, usually lies in the lower potential range.

## CONCLUSIONS

The addition of a NiFe-type catalyst layer significantly raised the photocurrent over the entire voltage range, and a minor cathodic shift for the onset potential of about 80–100 mV was observed. The photocurrents plateau above 1.3 V RHE and increased from ca. 1.9 to 2.5 mA/cm$^2$ at 1.23 V RHE after the addition of the catalyst layer. The cathodic current transient revealed the charge decay to be higher in the lower potential range (0.8–1.0 V RHE), but only with the deposited overlayer, pointing toward the ability of the catalyst to hold charges. Indeed, impedance analysis showed that the surface state capacitance ($C_{ss}$) increased by one order of magnitude, whereas the charge transfer resistance ($R_{ct,ss}$) remained unchanged when compared to that of the bare photoanode, thus confirming the hole storage capability of the catalyst layer. Moreover, the slightly reduced trapping resistance ($R_{trapping}$) indicates that the catalyst layer is able to efficiently extract holes from surface states of the hematite–titania photoanode. On the other hand, oxygen measurements at 1.23 V RHE unveiled a slightly better Faradaic efficiency after addition of the catalyst, possibly as a result of the higher applied potential compared to that in the impedance analysis. Thus, at higher potentials the oxidative power of the holes increases and the catalyst becomes more active toward OER.

Amorphous materials are prone to destabilization, which could be confirmed here after prolonged (48 h) electrolysis. Accordingly, it remains a trade-off to simultaneously optimize both functionalities, namely, high activity and long-term stability. At the same time, we need to emphasize that the conclusions drawn from our work cannot simply be extended to other photoactive materials because the functionality of the catalyst layer is not only dependent on its composition, porosity, and crystallinity but also on the photoactive material underneath. Nevertheless, our study provides a basis for understanding the interplay between photoactive materials and catalysts and may pave the way for further improvements, for example, by the addition of a catalyst that accelerates hole transfer to the solution at lower potentials.

## EXPERIMENTAL SECTION

### Preparation of Amorphous Iron Oxide Nanoparticles.

A microwave-assisted nonaqueous sol–gel route using Fe(acac)$_3$ (Sigma-Aldrich, ≥99.9%), benzyl alcohol (Sigma-Aldrich, anhydrous, 99.8%), and 1,3-propanediol (Alfa Aesar, 99%) was pursued as described in detail in ref 64. The particle size ranges from 2 to 4 nm according to a previously performed transmission electron microscopy analysis. The amorphous iron oxide nanoparticles were dispersed in methanol at a concentration of approximately 65 mg mL$^{-1}$.

### Preparation of Titania Nanoparticles.

The approximately 4 nm sized anatase titania nanoparticles were obtained using an oil bath synthesis. First, TiCl$_4$ (Aldrich, 99.9%) was dissolved in ethanol (Aldrich, ≥99.8%), followed by addition of BnOH and 1,3-propanediol. A detailed synthesis procedure can be found in ref 64.

### Preparation of Nanostructured Hematite–Titania Photoanodes.

Hematite–titania photoanodes were prepared by spin-coating mixed dispersions of amorphous iron oxide and anatase TiO$_2$ nanoparticles on F/SnO$_2$ substrates (7 Ω/sq) with a TiO$_2$ content of Ti (mol %)/[Ti (mol %) + Fe (mol %)] = 12%. The films were annealed at 750 °C at a ramp of 20 °C/min in a pure oxygen atmosphere for 20 min, followed by quenching in air. Energy-dispersive X-ray spectroscopy (EDX) analysis showed that the atomic percentage of Ti was 10.13% (Figure S16, SI). The hematite–titania photoanode without overlayer is abbreviated as bare-Fe$_2$O$_3$–TiO$_2$.

### Preparation of the Hematite–Titania–Fe$_{20}$Cr$_{40}$Ni$_{40}$O$_x$ Photoanodes.

The preparation of the overlayers was inspired by the deposition process used by Smith et al., however performed in a slightly different way: 2-ethylhexanoates of Fe$^{3+}$ (50 wt % in mineral spirits, Alfa Aesar, 214 μL), Cr$^{3+}$ (70 wt % in mineral spirits, ABCR Chemicals, 273 μL), and Ni$^{2+}$ (78 wt % in 2-ethylhexanoic acid, ABCR Chemicals, 184 μL) were dissolved in 7.6 mL of n-heptane (ACROS, >99%, extra dry), stirred for 2 h, and then centrifuged at 4000 rpm for 15 min to remove agglomerates prior to deposition. The solution was spin-coated on a hematite–titania photoanode at 3000 rpm for 60 s. The overlayered photoanode was then dried on a hot plate at 150 °C for 1 h. Infrared spectroscopy was employed to follow the thermochemical decomposition of the precursors. After the heat treatment, the C–H (2800–3000 cm$^{-1}$) and C–O (∼1680 cm$^{-1}$) vibrations disappeared, as shown for KBr disks coated with the precursor solution (Figure S6, SI). The thicknesses of the hematite–titania films and the OEC layers were in the range of 180–200 nm and about 100 nm, respectively, as determined by cross-sectional scanning electron microscopy (SEM) analysis (Figure S2, SI). However, after electrolysis, the thickness of the overlayer decreased drastically to <20 nm, as estimated by cross-sectional SEM analysis (Figure S3, SI). It is assumed that the catalyst covered the
entire surface of the porous photoanode. Elemental analysis of the precursor solution used for the deposited catalysts revealed a Fe/Ni/Cr atomic ratio of about 58:24:40 (Table S4, SI). The abbreviation over-Fe$_2$O$_3$−TiO$_2$ stands for the hematite−titania photoanode overlaid with such a FeNiCrO$_5$ layer.

Optical, Structural, and Morphological Film Characterization and Photoelectrochemical Measurements. X-ray photoelectron spectra (XPS) were recorded on a Sigma 2 spectrometer (Thermo scientific) using a nonmonochromated Al Ka X-ray source, where the binding energy was calibrated taking C 1s = 284.8 eV. EDX was performed on a Hitachi SU-70 scanning electron microscope operated at an acceleration voltage of 15 kV (Schottky-type field emission gun) and equipped with a X-Max 80 detector (Oxford Instruments). SEM analysis was performed on a Carl Zeiss LEO 1530 microscope equipped with a field emission gun operating at 3 kV. For the cross-sectional images, the photoanode was cut in the middle with a diamond knife. Fourier transform infrared (FT-IR) spectroscopy was performed on a Spectrum 100 FT-IR spectrometer from Tofwerk AG (model C-TOF) integrated on a VMP3 BioLogic potentiostat. Simulated AM 1.5 G solar irradiation was provided by an Oriel solar simulator equipped with a 300 W Xe lamp and AM 1.5 G solar irradiation was simulated using an I LN-725 integrating sphere accessory. Because the same sample was used for all measurements, no background correction was made. The acquisition parameters were as follows: scan speed 400 nm/min, change source at 340 nm, light source D2/WI, filter exchange step, correction baseline, vertical axis % T, and data interval 0.5 nm. Photoelectrochemical (PEC) measurements were recorded on a 1 M NaOH and degassed with argon prior to the measurements. The oxygen probe was inserted through a rubber septum, and continuous O$_2$ readings were conducted at 1 s interval throughout the experiment. The probe was calibrated using 2 points (argon: 0% O$_2$ and air: 20.9% O$_2$) with an error of 5% on the reading. Prior to the experiment, the baseline was measured for 30 min, followed by 10 min illumination with simulated AM 1.5 G irradiation (100 mW/cm$^2$) at 1.23 V$_{RHE}$. Oxygen leakage was subtracted by measuring the leakage rate before and after the measurement. Secondary ion mass spectrometry (SIMS) with high depth resolution was performed by means of a time-of-flight-mass spectrometer from Tofwerk AG (model C-TOF) integrated on a focused ion beam instrument (Lyra FIB) from Tescan. Low-impact-energy (5 keV) Ga$^+$ ions with a primary ion current of 180 pA were used for the elemental separation of the different layers.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.7b00696.

Additional photoelectrochemical measurements; SEM, XPS and transmittance measurements of films; Mott−Schottky plots; Nyquist plots; SIMS depths profiles; resistance data and elemental analyses (PDF)

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