Modification of Surface States of Hematite-Based Photoanodes by Submonolayer of TiO₂ for Enhanced Solar Water Splitting

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ABSTRACT: Surface states are inherently involved with photoelectrochemical (PEC) solar fuel production; some of them are beneficial and participate in the surface reactions, but some act as recombination centers and therefore limit the PEC efficiency. Surface treatments have been applied to modify the surface states, but interrelated effects of the treatments on both types of surface states have not been properly considered. This research examines the modification of the surface states on hematite-based photoanodes by atomic layer deposition of submonolayer amount of TiO₂ and by postannealing treatments. Our results show that the postannealing causes diffusion of Ti deeper into the hematite surface layers, which leads to an increased saturation photocurrent and an anodic shift in the photocurrent onset potential. Without postannealing, the separate TiO₂ phase on the hematite surface results in a second intermediate surface state and delayed charge carrier dynamics, i.e., passivation of the recombination surface states. It is evident by these results that the intermediate surface states observed with impedance spectroscopy in a PEC cell are directly involved in the surface reaction and not with the recombination surface states observed with ultrafast (picoseconds–nanoseconds) transient absorption spectroscopy in air. These results open new optimization strategies to control the beneficial and detrimental surface states independently.

INTRODUCTION

The increased energy demand has created a need for environmentally friendly energy production methods. Solar water splitting is a method to convert solar energy into hydrogen fuel directly at the semiconductor–electrolyte interface. Hematite (α-Fe₂O₃) is a promising material for solar fuel production: some of them are beneficial and participate in the surface reactions, but some act as recombination centers and therefore limit the PEC efficiency. Surface treatments have been applied to modify the surface states, but interrelated effects of the treatments on both types of surface states have not been properly considered. This research examines the modification of the surface states on hematite-based photoanodes by atomic layer deposition of submonolayer amount of TiO₂ and by postannealing treatments. Our results show that the postannealing causes diffusion of Ti deeper into the hematite surface layers, which leads to an increased saturation photocurrent and an anodic shift in the photocurrent onset potential. Without postannealing, the separate TiO₂ phase on the hematite surface results in a second intermediate surface state and delayed charge carrier dynamics, i.e., passivation of the recombination surface states. It is evident by these results that the intermediate surface states observed with impedance spectroscopy in a PEC cell are directly involved in the surface reaction and not with the recombination surface states observed with ultrafast (picoseconds–nanoseconds) transient absorption spectroscopy in air. These results open new optimization strategies to control the beneficial and detrimental surface states independently.
The effect of the surface states is thus unclear. The surface states and the charge transfer properties of the hematite–electrolyte interface can be modified by substituting a small amount of different material at the hematite surface.10,11 To optimize the water splitting efficiency, treatments that can modify the r-SS and i-SS independently are needed. However, many of the latest publications5,10,12 only consider passivation of the r-SS.

In this research, the effect of a submonolayer of ALD TiO2 deposited on hematite and the effect of the postannealing at 300–700 °C on the surface states were studied with photoelectron spectroscopy, transient absorption spectroscopy, and electrochemical impedance spectroscopy. Two different surface states were identified, one of which can be directly linked with the produced photocurrent and the water splitting reaction and the other one with the charge carrier recombination.

**EXPERIMENTAL SECTION**

Hematite thin films were fabricated on 25 × 10 × 1.1 mm² indium tin oxide (ITO)-coated glass substrates (Präzisions Glas & Optik, CEC020E, ITO coating (20 ± 5 ohm/sq) coated on EAGLE2000 boro-aluminosilicate glass) by an anodic electrodeposition. The electrolyte was a 1 M solution prepared from FeCl₃·4H₂O (Sigma-Aldrich, reagent grade, ≥98%), and the temperature of the electrolyte was kept at 60 °C during the electrodeposition. The electrodeposition was done at a constant potential of +1.2 V vs Ag/AgCl electrode (Harvard Apparatus, Leak-Free reference electrode 69-0023) by using an Autolab PGSTAT101 potentiostat. A charge of 60 mC/cm² was used in the electrodeposition, which corresponds to the film thickness of 60 nm. This was verified by XPS depth profiling shown in Figure S1. In the electrodeposition the Fe²⁺ ions oxidize and form FeOOH that was deposited on a 10 × 15 mm² area. FeOOH was then converted into hematite by annealing samples in a tube furnace (Carbolite Gero 30–3000 °C) at 750 °C for 8 h. The heating and cooling ramps were 5 and 1 °C/min, respectively. The formation of hematite was confirmed from the XRD patterns shown in Figure S2. In addition, the annealing induced a diffusion of In and Sn from the ITO substrate to the surface and a concurrent doping of the hematite layer with In and Sn as shown in Figure S3. This has been found to be beneficial to the photocurrent because of the increased charge carrier concentration.13–15

After the electrodeposition and annealing, two ALD cycles of TiO₂ were deposited on the top of the fabricated hematite films, which correspond to the average film thickness of 0.07 nm or 0.2 monolayers based on the growth per cycle determined from thinner films by ellipsometry (Rudolph Auto EL III ellipsometer, Rudolph Research Analytical). The deposition was performed at 200 °C in a Picosun Sunate ALD R200 Advanced reactor. Before starting the deposition the substrates were held in the reaction chamber for 30 min to stabilize the temperature. Tetrakis(dimethylamido)titanium-(IV) (TDMAT, electronic grade, 99.999+%, Sigma-Aldrich) and ultrapure Milli-Q water were used as precursors. During the deposition the TDMAT bubbler and the precursor gas delivery line was kept at 76 and 85 °C, respectively, to reach the proper vapor pressure and to prevent condensation of the precursor. The water was cooled to 18 °C with a Peltier element. Ar gas was used as a carrier/purge/venting gas (99.9999%, Oy AGA Ab). The continuous Ar flow in the TDMAT and water lines was 100 sccm. The deposition was started with the 1.6 s TDMAT pulse and was followed by the 0.1 s water pulse. Between each pulse the excess precursor was pumped during the 6.0 s purge period.

A total of 18 samples were fabricated, from which three without TiO₂ were used as reference. The remaining 15 samples were postannealed at 300, 400, 500, 600, and 700 °C for 1 h, three samples at each temperature, to verify the reproducibility of the measurements. We note that all the samples had been subject to a heat treatment at 750 °C before the TiO₂ deposition, and therefore the diffusion of In and Sn within the bulk of the hematite and the decrease in conductivity of the ITO substrate during the postannealing are assumed negligible. Annealing at 300 °C or higher temperatures provides reasonable stability of ALD TiO₂ during chopped light measurements under the water splitting condition (Figure S4).16

Equipment used for XPS measurements included an analysis chamber, a load lock chamber, an X-ray source (V. G. Microtech, 8025 twin anode X-ray source), and an energy analyzer with electron multiplier and detector (V. G. Microtech, CLAM4MCD LN05). All measurements were conducted by using X-ray source operated at 300 W power and Al anode (Al Ka, hν = 1486.7 eV). The pressure of the analysis chamber was below 2 × 10⁻⁸ mbar. XP spectra were calibrated so that the binding energy of the Fe²⁺ 2p½/peak is at 710.6 eV.

Electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV) were performed by using a three-electrode setup with an Ag/AgCl reference electrode (Harvard Apparatus, Leak-Free reference electrode 69-0023), a platinum wire counter electrode, and a sample as an working electrode (the diameter of the sample–electrolyte contact was 6 mm). The photoelectrochemical cell was filled with 3.5 mL of 1 M solution of NaOH (Sigma-Aldrich, sodium hydroxide, reagent grade) (pH 13.6). Measurements were done by an Autolab PGSTAT12 potentiostat (Metrohm AG) equipped with a...
frequency response analyzer (FRA2). The measured potential was converted to potential versus reversible hydrogen electrode (RHE) using the equation $V_{\text{RHE}} = V_{\text{Ag/AgCl}} + 0.197$ V + 0.0592 V × pH. The front side of the sample was illuminated through the electrolyte with an Asahi Spectra HAL-C100 solar simulator, and the intensity was calibrated by a 1 sun checker (Asahi Spectra CS-30).

Transient absorption spectra (TAS) of the Fe$_2$O$_3$/TiO$_2$ samples were measured by using a pump–probe setup with an excitation wavelength of 380 nm under ambient air conditions. The excitation density was roughly 1 μJ/cm$^2$. The primary laser pulses were obtained by using a Ti:sapphire laser (Libra F, Coherent Inc., 100 fs pulse at 1 kHz repetition rate). Most of the laser radiation was directed to a parametric amplifier (Topas C, Light Conversion Ltd.) to generate the pump pulses. Time-resolved transient absorption spectra were recorded by using ExciPro TA spectrometer (CDP, Inc.) in the wavelength range 430–730 nm.

### RESULTS AND DISCUSSION

#### Mixing of TiO$_2$ and Fe$_2$O$_3$ Layer.

The effect of the postannealing on the mixing of TiO$_2$ and the Fe$_2$O$_3$ layer was studied by XPS. The XP spectra were measured before and after the ALD TiO$_2$ deposition and after the postannealing. The Fe 2p$_{3/2}$ spectra were fitted with parameters described in ref 17 for hematite. The Fe 2p$_{3/2}$ and Ti 2p$_{3/2}$ spectra of Fe$_2$O$_3$/TiO$_2$ samples postannealed at 300 and 700 °C are presented in Figure 2. The binding energy of the Fe 2p$_{3/2}$ peak can be attributed to the oxidation state of 3+, and no changes in the Fe 2p peak shape were observed between samples. In contrast, the Ti$^{4+}$ 2p$_{3/2}$ peak shows a shift of −0.31 eV and a decrease in full width at half-maximum value from 1.78 to 1.47 eV as the postannealing temperature is increased from 300 to 700 °C. Spectra for other samples are presented in Figure S3.

For the postannealing temperatures higher than 500 °C the surface concentration of Ti decreases while the surface concentrations of In and Sn are increased (Figure 3). This indicates the diffusion of Ti at high temperatures from the surface into the top layer of hematite and the formation of mixed Fe$^{3+}$Ti$^{4+}$ surface oxide. The decreasing binding energy of the Ti 2p$_{3/2}$ peak with the increasing postannealing temperature follows the same trend with the Ti concentration. According to Hiltunen et al. 18 the binding energy of the Ti 2p$_{3/2}$ peak components corresponded to literature values for hematite. 19 The binding energies of the Sn 3d$_{5/2}$ and In 3d$_{5/2}$ peaks are fairly constant. A decrease of Ti and an increase of Fe, In, and Sn indicate that the Ti at the surface mixes with Fe$_2$O$_3$ surface layer during postannealing which is further supported by the decrease of the Ti 2p$_{3/2}$ binding energy.

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In 3d_{1/2}, do not change, which indicates that Sn and In stay in the same chemical environment (in Fe_{2}O_{3}) and that the chemical state does not change. At 700 °C the trend changes and the concentrations of In and Sn decrease slightly whereas the concentration of Fe increases.

Raman spectra showed no difference between the samples with submonolayer amount of ALD TiO_{2} (two cycles) and the Fe_{2}O_{3} reference due to the insufficient amount of TiO_{2}. However, an increase in LO peak (forbidden longitudinal optical mode) at 660 cm^{-1} was detected for bands with 15 ALD TiO_{2} cycles when film structure was postannealed at 750 °C (Figure S5). The increase in LO peak is linked with increase in the disorder in the crystal lattice. This supports the hypothesis of diffusion of Ti^{4+} into the hematite film. The structures of fabricated films were confirmed to be mesoporous by scanning electron microscopy (Figure S6). The morphology of the samples is not affected by the TiO_{2} deposition or postannealing treatments.

The band gap of the Fe_{2}O_{3}/TiO_{2} samples was defined by Tauc analysis (Figures S7 and S8). The indirect band gap was 2.1 eV for all samples, and neither the ALD TiO_{2} deposition nor the postannealing had any effect on the band gap.

**Surface States and Photocatalytic Properties.** Photoelectrochemical (PEC) measurements were performed to determine the photoresponse, chemical stability, and the charge transfer properties of the Fe_{2}O_{3}/TiO_{2} samples. PEC measurements included electrochemical impedance spectroscopy (EIS), linear sweep voltammetry (LSV), and chronoamperometric measurements. LSV curves are presented in Figures 4 and 7. TiO_{2} addition to the hematite surface and postannealing were found to increase the saturation photocurrent and shift the onset potential anodically.

The equivalent circuit presented in Figure 5 was used to model frequency response of the hematite-electrolyte interface. A similar equivalent circuit is commonly used for fitting impedance data. The circuit is the simplest equivalent circuit that can model the impedance response of the hematite-electrolyte interface with reasonable accuracy. The circuit consists of a constant phase element, a resistor, and a capacitor. The equivalent circuit is shown in Figure S9.

The flat-band potential was calculated from the EIS data by fitting the equivalent circuit (Figure 5) and doing Mott–Schottky analysis from C_{sc} component (Figure S9). Hematite is an n-type semiconductor, and a relative permittivity of 32 was used in the calculations. Obtained results are shown in Figure 6. The flat-band potential of hematite before the ALD deposition of TiO_{2} was 0.48 V vs RHE. The deposition increased and the postannealing at 400–600 °C decreased the flat-band potential. Similar flat-band potentials are reported in the literature for the hematite/1 M NaOH interface. The charge carrier density followed a similar trend compared to the flat-band potential. However, the charge carrier density drastically increased when the samples were postannealed at higher temperatures.
700 °C. We note that the information depth of XPS analysis corresponds to the depletion region width of the Fe$_2$O$_3$ photoanodes that was 4–6 nm based on the Mott–Schottky analysis. Thus, we assign the increase in the charge carrier density at 700 °C to the increased surface concentration of Fe$^{3+}$ shown in Figure 3.

The photocurrent onset potentials reported for hematite in the literature show strong variation ranging typically from +0.70 to +1.15 V vs RHE, and therefore it is challenging to compare absolute values with the literature. However, our values (+0.77 to +0.89 V vs RHE) fall within the range reported in the literature, and most importantly we were able to assign the anodic shift to the change in the surface composition. Furthermore, the largest variation in all results was observed for samples postannealed at 500 °C, which corresponds to the temperature range where surface composition changes strongly.

The photocurrent onset potential is directly related to the flat-band potential plus the overpotential needed to drive the water splitting reaction. A more cathodic flat-band potential causes larger band bending, resulting in better charge separation and thus lower charge recombination rate. The flat-band potential does not correlate with the photocurrent onset potential, which implies that the needed overpotential changes when TiO$_2$ is deposited on the hematite films and when films are postannealed. This anodic shift can be linked to the change in the i-SS.

The LDOS of the i-SS can be determined from the surface state capacitance. The filling of the surface states at certain potential is directly proportional to the capacitance $g(E) = C/\varphi$. The surface state capacitance $C_{ss}$ was obtained from the frequency response of the hematite–electrolyte interface (Figures S10–S21). The obtained surface state capacitance is shown in Figure 7, and the measurements were done in the dark and under 100 mW/cm$^2$ (1 sun) illumination with applied external bias voltage. Surface state capacitance was only observed when measurements were done under illumination. This indicates that filling or depleting of these states does not occur unless photons excite electron–hole pairs.

Two wide and low $C_{ss}$ peaks are observed in the case of the Fe$_2$O$_3$ sample while the $C_{ss}$ peaks are much more distinct for the Fe$_2$O$_3$/TiO$_2$ samples postannealed at 300 °C. Similar results are reported in the literature, and it was discovered that the deposition of a different material on top of the hematite films, such as Al$_2$O$_3$, produces two distinct peaks. Postannealing at 500 °C or higher temperatures causes the right peak to disappear and the left peak to move to the more anodic potential. The photocurrent onset is at the potential corresponding the maximum of the left $C_{ss}$ peak, and the onset potential and peak positions change equally. The height of the peak is larger for samples postannealed at 500 °C or higher temperatures. For these samples the photocurrent onset is also sharper, and from these results it can be concluded that the left $C_{ss}$ peak is related to the photocurrent onset potential and thus to the water splitting charge transfer reaction. The i-SS can be described by Tamm states which are induced by unsaturated oxygen at the surface. These states exist just above valence band.

The right peak does not shift but is superimposed when the postannealing temperature is higher than 500 °C. Similar double peaks were reported in the literature for Al$_2$O$_3$-coated electrodes, and presumably this capacitance peak can be attributed to two different surface phases. The mixing of TiO$_2$ and Fe$_2$O$_3$ layers causes the peaks to combine.

The r-SS is difficult to detect by impedance spectroscopy because no charge transfer takes place through these states. The r-SS was studied by TAS. The measurements were done in air without electrolyte, and therefore the data do not provide information about the i-SS. Instead, the differences in TAS spectra can be compared and be linked with the material properties of hematite. The trapping and recombination of charge carriers take place at the picoseconds–nanoseconds time scale, which is significantly faster than the charge transfer (~1 s time scale) across the hematite–electrolyte interface. The recombination dynamics in hematite probed by TAS in the microseconds–milliseconds time scale at 580 nm has been reported to be insensitive to the electrode environment. For these reasons, the TAS measurements conducted in the absence of electrolyte provide here information about the charge carrier dynamics of the r-SS in the hematite films.

To compare charge carrier dynamics between the samples, the TAS spectra were normalized at a delay time of 0.2 ps (Figure 8 and Figure S22). The spectra featured a strong peak at 570 nm, which is also reported in the literature for measurements done under electrolyte conditions. The wavelength corresponds to an electron transition of 2.1 eV from the top of the valence band to the localized states just below the conduction band.
Figure 7 are not due to the charge carrier dynamics associated during the water splitting reaction. The surface state capacitance are involved with the charge transfer that the intermediate surface states (i-SS) probed via the absorption at 570 nm to the r-SS in Fe₂O₃. The sample the disappearance of the free carriers and the remaining absorption response. However, at longer delay times the spectral difference becomes more pronounced. At 570 nm the signal is on the level of 0.2–0.3 relative to that at 0.2 ps, and even stronger decay can be seen in the red side of the spectrum at wavelengths longer than 640 nm. As a rough approximation, an almost complete decay in the red part can be attributed to the disappearance of the free carriers and the remaining absorption at 570 nm to the r-SS in Fe₂O₃. The sample postannealed at 300 °C shows the least degree of recombination of free carriers and the highest r-SS population at 1 ns delay time. Interestingly, the charge carrier lifetime is prolonged only when there exists a separate TiO₂ phase at the hematite surface, and the charge carrier concentration in the trap states is thus higher. From this it can be concluded that TiO₂ clearly modifies the r-SS. In general, the increased charge carrier lifetime increases the probability of the charge carriers to take part in the water splitting reaction.

The TAS results confirmed the successful passivation of the r-SS by the TiO₂ phase. Strikingly, no difference in the TAS signals was observed between the sample with Ti diffused into the hematite surface and the hematite reference. This suggests that the differences in the PEC performance presented in Figure 7 are not due to the charge carrier dynamics associated with the r-SS. In contrast, these results support the hypothesis that the intermediate surface states (i-SS) probed via the surface state capacitance are involved with the charge transfer during the water splitting reaction.

■ CONCLUSIONS
The surface states of the hematite photoanodes take part in the charge carrier transfer, trapping, and recombination processes during the solar water splitting reaction, having a significant impact on the photocatalytic efficiency. The modification of the hematite surface states by a submonolayer of ALD TiO₂ was studied by impedance spectroscopy and transient absorption spectroscopy. The results show that the surface states are a necessary intermediate step in water splitting reaction, and the charge transfer can only take place when holes are occupying the intermediate surface states (i-SS). The potential of the i-SS affects the photocurrent onset potential, and the LDOS of i-SS affects the amount of generated photocurrent, thus corresponding to the sharpness of the photocurrent onset. Two different surface phases (Fe₂O₃ and TiO₂) give rise to two distinct surface state capacitance peaks. Postannealing causes the mixing of the layers and thus the merging of the i-SS peaks. Unfortunately, this also shifts the LDOS of the i-SS and the photocurrent onset to the anodic direction, which decreases the overall water splitting efficiency. The charge carrier lifetime in recombination surface states (r-SS) is increased when a separate TiO₂ phase exists at the hematite surface, which results in an efficient passivation of these detrimental surface states.

This work provides a deeper understanding on the type and role of surface states in photoelectrochemical water oxidation on hematite-based photoanodes. The effects of the beneficial intermediate surface states and detrimental recombination surface states to the overall water splitting efficiency seem to be uncorrelated, which opens new optimization strategies to the photoelectrode surface treatments.

■ ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c00798.

Material characterization results (PDF)

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Notes
The authors declare no competing financial interest.

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