Influence of Ti Doping Levels on the Photoelectrochemical Properties of Thin Film Hematite (α-Fe₂O₃) Photoanodes

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ABSTRACT: Doping with Ti enhances the electron conductivity in hematite (α -Fe₂O₃) photoanodes, as well as their photoelectrochemical properties with respect to undoped hematite photoanodes. However, the optimal doping level is unknown. This work examines the influence of the Ti doping level on the photoelectrochemical properties of thin (\sim 50 nm) film hematite photoanodes. The films were deposited by pulsed lased deposition (PLD) on glass substrates coated with transparent electrodes (fluorinated tin oxide, FTO) from Ti-doped Fe₂O₃ targets with different Ti concentrations: 0 (undoped), 0.25, 0.8, 1 and 7 cation%. The film thickness, morphology, microstructure and optical properties were nearly the same for all the photoanodes, thereby enabling systematic comparison of the effect of doping level without spurious side effects related to morphological variations. The photoelectrochemical performance of all of the Ti-doped photoanodes was considerably higher than the undoped photoanode. Among the doped photoanodes, the performance of the heavily-doped (7%) photoanode was found to be lower than the other photoanodes with doping levels $\leq 1\%$. Complementary measurements with a hole scavenger (H₂O₂) and intensity modulated photocurrent spectroscopy (IMPS) analysis show that for the doped photoanodes both the charge separation and charge transfer efficiencies improved with decreasing doping levels, and they were considerably lower for the heavily-doped photoanode than for the lightly-doped photoanodes.

1. INTRODUCTION

Research on solar energy conversion and storage by means of photoelectrochemical (PEC) water splitting has bloomed since Fujishima and Honda's seminal work on TiO_2 ¹. Research in this field is motivated by the hope that PEC solar water splitting could potentially lead to a new technology for scalable production of hydrogen-based fuels from renewable sources, providing a

sustainable alternative to fossil fuels ². The most critical challenge towards the development of this promising technology is, currently, the development of inexpensive, efficient, stable and durable photoanodes for water photo-oxidation. Hematite (α -Fe₂O₃) has emerged as a leading candidate among the prospective materials for water photo-oxidation ³. Hematite is cheap, abundant, stable in alkaline aqueous solutions and has a band gap energy of 2.1 eV which is nearly optimal for solar water splitting, especially in tandem with Si PV cells.³ Water photo-oxidation current (photocurrent, in short) densities of *ca*. 4 and 6 mA/cm² were reported recently for ultrathin (26 nm) compact film ⁴ or nanostructured thick (~500 nm) layers ⁵ doped with Ti or Ru, respectively. This is still significantly lower than the theoretical limit of 12.6 mA/cm² for hematite under standard solar illumination condition (AM1.5G). Likewise, efforts to reduce the external voltage that must be applied in order to drive the complete water splitting reaction show promising results in lowering the onset potential of hematite photoanodes through the use of cocatalysts ⁶, overlayers ⁷ and other surface modifications ⁸. But here too there is still much room for further improvement ⁹.

Doping is a powerful handle to tailor the electrical properties of metal-oxides in general ¹⁰, and hematite photoanodes in particular ¹¹. Substituting Fe(III) with high valent cations such as Si(IV) or Ti(IV) enhances the electron concentration and *n*-type conductivity in hematite ¹². Thin film hematite photoanodes doped with Si or Ti display markedly enhanced activity towards water photo-oxidation than their undoped counterparts ¹³. However, the effect of different dopants and doping levels on the photoelectrochemical properties of hematite photoanodes remains unknown, for the most part. Although many reports on hematite photoanodes have been published, especially in the last decade, it is very difficult to make unambiguous conclusions on the effect of doping because different studies examined photoanodes with markedly different

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microstructures and morphologies and it is impossible to decouple these spurious side effects from the influence of doping on the electrical and photoelectrochemical properties of the photoanodes. In order to overcome this difficulty we study thin (~50 nm) film hematite photoanodes with compact polycrystalline morphology. The films are produced by pulsed laser deposition (PLD) under precisely controlled conditions that ensure high reproducibility ¹⁴ which is the key for systematic investigations. Recently, we reported the results of a comparative investigation of the effect of different dopants (Sn, Ti, Nb, Zn, Si, Pt, Zr, Ni and Mn) at a fixed doping level of 1 cation% ¹⁵. Here in this work we report the influence of the doping level (concentration) of one of these dopants, Ti, on the water photo-oxidation performance. Ti is a commonly used dopant in hematite photoanodes ^{4 16 17}. Previous studies on Ti-doped hematite photoanodes investigated mesoporous layers with high Ti concentrations above the solubility limit ¹⁸, making it difficult to decouple the effect of doping from spurious microstructural and segregation effects.

In this work we examine the influence of Ti doping at low concentrations (< 1 cation%), for the most part, and compare them with undoped and heavily-doped (7 cation%) photoanodes. We also take care to insure that the microstructure of the films remains nearly the same, independent of the doping level. This is essential for systematic investigation of doping effects, as demonstrated in our previous study of different dopants ¹⁵. We present comprehensive microstructural analysis of the photoanodes and a systematic comparison of their photoelectrochemical performance.

2. EXPERIMENTAL SECTION

Photoanode preparation: Thin (~50 nm) film hematite photoanodes were prepared by pulsed laser deposition (PLD) on fluorinated tin oxide (FTO) coated soda lime glass substrate (TEC15, Pilkington) that had been cleaned before the deposition to insure reproducible results as reported elsewhere ¹⁴. The films were deposited from iron oxide targets with different Ti concentrations: 0 (undoped), 0.25, 0.8, 1 and 7 cation%. The targets were prepared by solid state reaction of high purity powders of Fe₂O₃ (99.99%, Alfa Aesar) and TiO₂ (99.995%, Alfa Aesar) that were mixed in appropriate amounts in order to obtain Ti concentrations of 0 (undoped), 0.25, 0.8, 1, and 7 cation% (i.e., Ti / (Ti + Fe)). The powders were thoroughly mixed using mortar and pestle and the mixed powder was ball-milled for 24 h using YTZ milling balls (Tosoh, Japan), and subsequently pressed in a stainless steel mold and sintered in air at 1200 °C for 12 h, resulting in a 1" disk-shaped pellet, which was used as a target for the film deposition.

The deposition was carried out using a PLD system (2" PLD Workstation, Surface Systems & Technology) equipped with a KrF ($\lambda = 248$ nm) excimer laser (COMPexPro 102, Coherent). All the films were deposited using 9000 laser pulses with a fluence of 1 J/cm² and repetition rate of 3 Hz, which corresponds to a film thickness of ~50 nm. The distance between the substrate and the target was 70 mm, and the heater set-point temperature was 500 °C which corresponds to a substrate temperature of approximately 450 °C. The deposition was carried out in O₂ gas atmosphere at a constant pressure of 25 mTorr.

Characterization: The surface morphology of the hematite films was examined using field emission scanning electron microscopy (FESEM, Zeiss Ultra-plus) under identical observation conditions. The composition of the targets was measured using a FEI Quanta 200 SEM equipped with an Oxford WDS detector. The surface roughness was analyzed by atomic force microscopy (AFM, Park Systems XE-70). X-ray diffraction (XRD) patterns of all the photoanodes were collected using an X-ray diffractometer (Rigaku, Smartlab) in parallel beam configuration with Cu K α radiation in the 2 θ range of 20 to 75° at a scan rate of 0.01°/s.

The optical properties of all the photoanodes were obtained by spectrophotometric measurements in diffuse-reflection and transmission modes using an Agilent Cary 5000 spectrophotometer equipped with an integrating sphere. Photoelectrochemical measurements were carried out in an electrochemical cell known as the "cappuccino cell" in three electrode configuration ¹⁴. The photoanode served as the working electrode, a platinum wire served as the counter electrode, and an Ag/AgCl electrode in saturated KCl solution served as the reference electrode. The electrodes were immersed in 1M NaOH aqueous solution ($pH = 13.6 \pm 0.1$, measured by a pH meter, pH700 from EUTECH Instruments) inside the cappuccino cell. Current vs. potential (J-U) linear sweep voltammograms were measured in the dark and under illumination at a potential ramp rate of 10 mV/s, and chopped light chronoamperometry measurements were carried out with 3 s exposure intervals. These measurements were carried out using a potentiostat (Ivium CompacStat) set in the three electrode mode configuration. The photoanodes were illuminated from the front side using a solar simulator (ABET Technologies Sun 3000 class AAA solar simulator). Further details are provided elsewhere ¹⁴. In order to separate between charge separation and extraction processes within the photoanode and at the surface, respectively, intensity modulated photocurrent spectroscopy (IMPS) measurements were performed using a Zahner Zennium electrochemical workstation equipped with a CIMPS system. The light source was a high-power white light emitting diode (Zahner WLC01 LED). IMPS measurements and analysis are discussed elsewhere¹⁹.

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3. RESULTS

Wavelength dispersive X-ray spectroscopy (WDS) was used for accurate measurement of the Ti concentration in the doped targets. The results of doped targets are listed in Table 1. In case of the undoped target, the concentrations of Ti and Si, the most common impurity in iron ores, was below the detection limit (20 and 27 ppm, respectively) with the confidence level of 95% (2σ), see Table S1. Figure 1 shows a photograph of all the photoanodes after photoelectrochemical measurements. The color of the films is uniform and no visible signs of degradation are observed. The visible circular mark on the undoped and 1% Ti-doped photoanodes is the mark of the O-ring that was used to seal the photoanodes in the cappuccino cell. Figure 2 shows high resolution scanning electron microscopy (HRSEM) images of the photoanodes. The surface morphology of all the photoanodes is identical and mimics the surface morphology of the FTO-coated glass substrates, which indicates conformal coating.

Target	Ti concentration (cation %)
0.25% Ti	0.25±0.01
0.8% Ti	$0.82{\pm}0.08$
1% Ti	1.10±0.05
7% Ti	$6.8{\pm}0.8$

Table 1. Ti concentration in the doped targets.



Figure 1. Photograph of hematite photoanodes with Ti doping levels of 0 (undoped), 0.25, 0.8, 1

or 7%.



Figure 2. HRSEM images of hematite photoanodes with Ti doping levels of (a) 0 (undoped), (b) 0.25, (c) 0.8, (d) 1, and (e) 7%. The scale bars correspond to 200 nm.

AFM images of the photoanodes show similar polycrystalline morphology that replicates the FTO-coated glass substrates underneath the hematite films, indicating uniform coverage of the films (Figure 3). The average surface roughness is nearly identical for all the photoanodes (Figure 3(f)).



Figure 3. AFM images of hematite photoanodes with Ti doping levels of (a) 0 (undoped), (b) 0.25, (c) 0.8, (d) 1 and (e) 7%. (f) The average roughness values of all the photoanodes.

Figure 4 shows XRD patterns of all the photoanodes. The labeled peaks correspond to Bragg reflections from the α -Fe₂O₃ hematite phase (JCPDS 01-080-5413) and SnO₂ rutile phase (JCPDS 01-079-6887). No other phases were identified in the diffractograms. The domain size calculated by the Scherrer formula from the (110) reflection of the hematite was nearly the same (~9-12 nm) for all the photoanodes.



Figure 4. XRD pattern of hematite photoanodes with different Ti doping levels as indicated right next to each curve. The Bragg reflections of the α -Fe₂O₃ hematite and SnO₂ rutile phases are indexed at the top part of the figure.

Figure 5 shows optical absorptance spectra of the photoanodes, and of a FTO-coated glass substrate without hematite (for comparison). The absorptance was calculated using the formula A = I - R - T, where R and T are the reflectance and transmittance spectra measured using a spectrophotometer equipped with an integrating sphere. The hematite photoanodes absorb light at wavelengths below 600 nm, which correspond to the absorption edge of hematite. The absorptance spectra of all the photoanodes are similar and much higher than that of the FTO-coated glass substrate at all wavelengths.



Figure 5. Absorptance spectra of hematite photoanodes with different Ti doping levels and a bare FTO-coated glass substrate. The doping levels are indicated in the legend.

The flat-band potential (U_{fb}) and dopant density (N_d) were calculated by Mott-Schottky analysis of capacitance vs. potential (C-U) measurements ²⁰. The analysis accounts for the Helmholtz capacitance (C_H) according to the following expression ²¹:

$$\frac{1}{c^2} = \frac{2}{N_d e_{\mathcal{E}_r \mathcal{E}_o} A^2} \cdot \left[U_{fb} + U \right] + \frac{1}{c_H^2} \tag{1}$$

where e is the elementary charge, ε_{a} the permittivity of free space, $\varepsilon_{r} = 33$ the relative dielectric constant of hematite 22 and A is the surface area of the photoanode exposed to the electrolyte. The exposed area within the cappuccino cell (0.28 cm²) is corrected by accounting for the surface roughness measured by the AFM (see Figure S1). The value of the Helmholtz capacitance used in the present analysis is $C_H = 10 \ \mu\text{F/cm}^{2\ 21}$. Figure 6(a) shows the I/C^2 vs. U plots of the 0.25% Ti-doped photoanode, measured at a frequency of 1000 Hz in 1 M NaOH aqueous solution with and without hole scavenger $(0.5 \text{ M H}_2\text{O}_2)$. The two plots measured with and without H_2O_2 yield nearly the same results, indicating that the capacity measured at this frequency is the space charge capacity rather than surface state capacity. The intercept and slope of the straight line fitting of the data yield the flat-band potential and dopant density, respectively (see equation 1). Similar Mott-Schottky analyses were performed for all the photoanodes at frequencies between 200 Hz and 25 kHz (see Table S2 in supplementary information for a list of all the frequencies at which the capacitance was measured). All the C-U measurements in this frequency range yielded linear Mott-Schottky plots, as in Figure 6(a), except for the undoped specimen that displays an odd shaped $1/C^2$ vs. U curve that could not be fitted with straight line as shown in Figure S2. Therefore the Mott-Schottky analysis was applied only for the doped specimens. The spread in the U_{fb} and N_d values in Figures 6(b) and (c), respectively, corresponds to measurements at different frequencies. The flat-band potentials were found to be between 0.3

to 0.4 V_{RHE} for all the doped photoanodes except for the heavily-doped (7%) one for which it was higher (~0.6 V_{RHE}). The dopant density increases from 9×10¹⁹ cm⁻³ for the lowest doping level (0.25%) to 1.2×10²¹ cm⁻³ for the highest doping level (7%).



Figure 6. (a) Mott-Schottky plots of the 0.25% Ti-doped hematite photoanode, measured at 1000 Hz in 1 M NaOH aqueous solution with and without 0.5 M H₂O₂ (orange and blue circles, respectively). (b) Flat-band potentials and (c) dopant densities as a function of the nominal doping level.

The photoelectrochemical properties of the 0 (undoped), 0.25, 0.8, 1 and 7% Ti-doped photoanodes are shown in Figure 7. Figure 7(a) shows the light and dark *J*-*U* voltammograms of all the photoanodes measured in 1 M NaOH aqueous solution without additional reagents. Therefore, the currents in Figure 7(a) correspond to water oxidation. Figure 7(b) shows the photocurrent, that is the difference between the light and dark currents ($J_{photo} = J_{light} - J_{dork}$), as a function of the applied potential. The photocurrent was found to decrease with increasing doping levels. Figure 7(c) shows voltammetry measurement in 1 M NaOH aqueous solution with a hole scavenger (0.5 M H₂O₂) ²³. Chopped light measurements of the respective photoanodes in 1 M NaOH with and without hole scavenger (0.5 M H₂O₂) are presented in the supplementary information (Figures S3, S4). The undoped specimen displays the lowest photocurrent and highest onset potential of all the photoanodes. The best performance was achieved by the lightly Ti-doped (0.25%) specimen that displayed the highest photocurrent and lowest onset potential of all the photoanodes. The tendency of the photocurrent as a function of the doping level is similar with or without the hole scavenger (compare Figure 7(d) and 7(b), respectively).



Figure 7. Light (solid line curves) and dark (dashed line curves) voltammograms of all the photoanodes, measured in 1 M NaOH aqueous solution without (a) and with (c) 0.5 M H₂O₂. Figures (b) and (d) present the water and H₂O₂ photocurrents, respectively, obtained by subtracting the dark currents from the light currents. Different line colors correspond to different doping levels as indicated in the legends.

IMPS analysis of the 0 (undoped), 0.25, 1 and 7% Ti-doped hematite photoanodes is presented in Figure 8. The theory behind this analysis is explained in detail elsewhere¹⁹. On the basis of 15 IMPS spectra per sample, the positive hole current and the negative surface recombination current were determined, as demonstrated in the supplementary information (Figures S5, S6). The three curves for each sample in Figure 8 are the photocurrent (solid lines), the hole current (dashed lines) and the surface recombination current (dotted lines). One can see that the hole current is significantly larger for the lightly-doped (0.25%) photoanode than for the other photoanodes. Also, the slope of the hole current for the heavily-doped (7%) photoanode is steeper than for the other photoanodes, but the hole current remains the lowest in the entire potential range. The extrapolated hole currents intersect with the x-axis at higher potentials for higher doping levels; 0.4, 0,7 and 0.9 V_{RHE} for the 0.25, 1 and 7% Ti-doped photoanodes, respectively (see Figure S7). With increasing doping levels the maxima in the magnitude of the recombination current (dotted lines) are shifted to higher potentials: 1.30, 1.33 and 1.43 V_{RHE} for the 0.25, 1 and 7% Ti-doped photoanodes, respectively. A similar trend is also observed in the rise-on potentials. The hole current of the undoped sample is much smaller than the doped samples, and it is matched by the recombination current up to ~ 1.5 V_{RHE}.



Figure 8. Photocurrent (solid line curves), hole current (dashed line curves) and recombination current (dotted line curves) for the 0 (undoped), 0.25, 1 and 7% Ti-doped photoanodes as determined by IMPS analysis.

4. DISCUSSION

The morphology of all the photoanodes and their absorptance spectra are nearly the same, regardless of the doping level. Therefore, differences in the photoelectrochemical properties can be safely assigned to electronic and photoelectrochemical effects induced by different doping levels rather than spurious side effects arising from morphological variations. The results of the photoelectrochemical measurements (Figure 7) with and without hole scavenger (H₂O₂) and the hole current determined by IMPS analysis (Figure 8) show similar trends: in both cases the photocurrent increases with decreasing doping levels, except for the undoped specimen that displays the lowest photocurrent and highest onset potentials of all of the photoanodes. This indicates that for the doped specimens the charge separation efficiency increases with decreasing doping levels ²³, caused by bulk effects. Surface effects are mostly determined by the competition between charge extraction and surface recombination and can be assessed by the charge transfer efficiency, η_t (= photocurrent / hole current) ¹⁹. The charge transfer efficiency can be easily calculated from the results in Figure 8 and is shown in Figure 9 for the 0 (undoped), 0.25, 1 and 7% Ti-doped photoanodes.



Figure 9. Charge transfer efficiency for the 0 (undoped), 0.25, 1 and 7% Ti-doped photoanodes as determined by IMPS analysis of the results in Figure 8.

The undoped sample displays much lower charge transfer efficiency than all of the other photoanodes. Among the doped photoanodes, the lightly-doped ones with doping levels of 0.25

or 1% display similar charge transfer efficiencies, whereas the charge transfer efficiency of the heavily-doped (7%) photoanode is significantly lower at all potentials (except for the highest potentials, around 1.6 V_{RHE} , where the difference becomes less distinct). Thus, we conclude that the lower performance of the heavily-doped photoanode results from both bulk and surface effects that give rise to lower hole current and lower charge transfer efficiency, at all potentials.

The influence of the doping level on benchmark parameters defined elsewhere ¹⁵ were extracted from Figure 7(b), as shown in Figure 10(a) for the case of the 0.25% Ti-doped photoanode where we demonstrate how the photovoltage (V_{photo}) and photocurrent (J_{photo}) are obtained at one point ($J = 0.4 \text{ mA/cm}^2$). Figure 10(b) presents the power characteristics of the photoanode (J_{photo} vs. V_{photo} , similarly to photovoltaics), and Figure 10(c) shows the intrinsic solar to chemical conversion (*ISTC*) efficiency as a function of J_{photo} . The maximum *ISTC* value (*ISTC_{max}*) for this photoanode is 0.1, obtained at a potential $U_{light}(ISTC_{max})$ of 1.5 V_{RHE}. The figure of merit (*FOM*) for this photoanode is 0.09, as defined elsewhere ¹⁵.

$$FOM = \frac{ISTC_{max}}{U_{light}(ISTC_{max})/1.23[V_{RHE}]}$$
(2)



Figure 10. (a) Light and dark voltammograms for the 0.25% Ti-doped hematite photoanode showing how J_{photo} , V_{photo} and other benchmark parameters are extracted. (b) J_{photo} vs. V_{photo} . (c) ISTC vs. J_{photo} .

Similar calculations were made for all the photoanodes except for the undoped one that displayed very low photocurrent and high onset potential (~1.5 V_{RHE}). The results are summarized in Figure 11, showing (a) the maximum photocurrent $(J_{photo,max})$; (b) the photocurrent at the reversible potential $(J_{photo @ 1.23})$; (c) the photocurrent at the thermoneutral potential $(J_{photo @ 1.48})$; (d) the rise-one potential where J_{photo} reaches 0.1 mA/cm² ($U_{rise-on}$); (e) the maximum photovoltage $(V_{photo,max})$, and (f) the figure of merit (FOM) for all the photoanodes. The benchmark parameters of the photoanode with the highest doping level (7%) are considerably lower than those of the other doped photoanodes: the photocurrent and photovoltage are smaller and the rise-on potential is higher than for the other doped photoanodes. This is consistent with the rather poor charge separation efficiency and high flat-band potential of the heavily-doped photoanode, see Figures 7(d) and 6(b), respectively. The other doped photoanodes, with doping levels $\leq 1\%$, display quite similar benchmarks and the differences are too small to tell if there is a favorite doping level in this range of doping levels. Based on these results we conclude that high doping levels exceeding 1 cation% degrade the photoelectrochemical performance of thin film hematite photoanodes with compact polycrystalline morphology.



Figure 11. Comparison of all the photoanodes with respect to the following benchmark parameters: (a) *J*_{photo,max}, (b) *J*_{photo @ 1.23}, (c) *J*_{photo @ 1.48}, (d) *U*_{rise-on}, (e) *V*_{photo,max} and (f) *FOM*.

5. CONCLUSIONS

Doping with Ti improves the photoelectrochemical properties of hematite photoanodes for water photo-oxidation, with respect to undoped counterpart photoanodes. However, this study shows that the optimal doping level for compact thin (50 nm) films on FTO-coated glass substrates is below 1 cation%. Higher doping levels exceeding 1 cation% degrade both the charge separation and charge transfer efficiencies and shift the flat-band and rise-on potentials to higher potentials, compared to lightly doped counterpart photoanodes. These results disagree with previous studies on mesoporous thick film hematite photoanodes that reported much higher optimal doping levels (e.g., 10 cation% in Ref. 17). This discrepancy result, most likely, from the different fabrication methods that give rise to markedly different morphologies of the respective photoanodes, showing the intricate nature of several effects – both electrical, electrochemical and morphological ones – of doping on the performance of hematite photoanodes for solar water splitting.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.

- AFM analysis of the geometrical and actual surface roughness of the photoanodes.
- Chopped-light and linear sweep voltammetry measurement of photoanodes in 1M NaOH without and with hole scavenger (0.5 M H₂O₂).
- IMPS spectra and analysis for the 1% Ti-doped hematite photoanode.
- Selected frequencies used for capacitance voltage and Mott-Schottky analysis of the hematite photoanodes.

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TOC graphics:

