Yttrium-doped hematite photoanodes for solar water splitting: Photoelectrochemical and electronic properties

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We investigate yttrium-doped hematite thin-film photoelectrochemical properties and find yttrium incorporation to amply improve the performance as a photoanode for water splitting under visible light. We used the spray pyrolysis method to prepare a set of yttrium doped Fe\textsubscript{2-x}Y\textsubscript{x}O\textsubscript{3} (x = 0, 0.05, 0.10, 0.15, 0.2) thin films (thickness below 500 nm) on glass and transparent conductive oxide coated glass slides. Using a substitutional homovalent (Y\textsuperscript{3+}) dopant, the effect on functionality is rationalised as a combined effect on the electronic structure and small polaron mobility from the lattice structure, impurity levels, lattice stability and variance in hybridisation. The photoelectrochemical response measurements indicate highest performance at Fe\textsubscript{1.9}Y\textsubscript{0.1}O\textsubscript{3} composition.

1. Introduction

Photoelectrochemical cells based on semiconductor electrodes convert light energy directly to chemical energy by splitting water into hydrogen and oxygen gases \cite{1} as demonstrated in Fig. 1. The feasibility of using TiO\textsubscript{2} as a semiconductor photoanode for water splitting was first experimentally demonstrated by Akira Fujishima and Kenichi Honda in 1972 \cite{2}. In this process, electrons photoexcited into the conduction band (CB) are extracted towards a counter-electrode to promote the hydrogen reduction reaction, while the photo-produced holes in the valence band participate locally at the anode in the reaction of water to form oxygen \cite{3,4}. The half reactions on anode and cathode in PEC are as follows, respectively:

\begin{align*}
2e^- + 2H_2O &\rightarrow H_2 + 2OH^- \quad (1) \\
2h^+ + 2OH^- &\rightarrow 1/2O_2 + H_2O \quad (2)
\end{align*}

Later on many different materials has been tested for photoanodes in PEC. The most promising photoanode materials are TiO\textsubscript{2}, α-Fe\textsubscript{2}O\textsubscript{3}, BiVO\textsubscript{4} and CdS, as well as group III-V semiconductors, such as GaAs and InP \cite{5}. Hematite (α-Fe\textsubscript{2}O\textsubscript{3}) is great candidate to be used as photoanode, because it has a narrow optical band-gap of 1.9–2.3 eV \cite{5}, chemical stability and earth-abundancy \cite{6,7}. Till now a record performance for hematite photoanode 4.32 mA/cm\textsuperscript{2} at 1.23 V versus reversible hydrogen electrode has been observed by Pt-doped α-Fe\textsubscript{2}O\textsubscript{3} decorated Co-Pt \cite{8}. This photocurrent corresponds to approximately 34% of the theoretical solar to hydrogen efficiency for hematite with a band gap of 2.1 eV \cite{8}.

Photoelectrochemical performance for hematite can be improved by doping with large variety of metal ions \cite{9–26}. Dopants mainly modify the width and redox potential of band gap or improve small polaron mobility due to hematite lattice contraction \cite{24,25}. The aim of the present investigation is to experimentally characterise the influence of Y\textsuperscript{3+} loading on the structure and photoelectrochemical properties of hematite, which, in best of our knowledge, has not been reported before. Y is a BIII group element with an electron configuration of 4d\textsuperscript{5}s\textsuperscript{2} and oxidation state of 3\textsuperscript{+}. Yttrium 3\textsuperscript{+} in yttrium-stabilized zirconia is known as the optimal catalyst to reduce the energy barriers in the reactions to produce higher hydrocarbons \cite{27}, and is indispensable in high temperature oxygen sensors for exhaust gases and high temperature solid oxide fuel cells \cite{28}. Influence on photocatalytic properties of dopant Y\textsuperscript{3+} has been studied in titania, titanate, vanadate compounds \cite{29,30} where it is an aliovalent-cation (hole) dopant and more straightforwardly can be seen to produce acceptor sites, but not in hematite where the Y\textsuperscript{3+} dopant is homovalent with the host lattice.

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cation. Nevertheless, whereas aliovalent dopants are naturally prone to introduce lattice defects (e.g. oxygen vacancies, which can facilitate recombination of photoexcited charge and therefore deteriorate charge transport), the alignment of (valence) bands of host and homovalent-dopant may in favourable configurations provide a better stabilised improvement, though via more intricate approach. Further, the relatively large ionic radius of $Y^{3+}$ can either stabilise (as e.g. in yttrium stabilised zirconia) or create contracted counterparts of hematite lattice, which may have an effect on small polaron mobility. Polaron mobility in hematite depends from Fe-Fe distance [24]. The lattice strain in the form of reduced Fe-Fe distance increases polaron mobility [24]. Also, introducing non-magnetic cations into an antiferromagnetically ordered hematite lattice may have a secondary effect on charge transport properties, because the electron conduction in hematite essentially occurs along the same layers where all the Fe atoms have the same magnetic moment [24]. The summary effect therefore has a number of sources, the interplay of which (and even a dominating factor) are not trivially obtainable from theory [24,25].

Different methods have been applied to obtain thin film hematite photoanodes, including atmospheric pressure chemical vapour deposition [31,32], aerosol-assisted chemical vapour deposition [33], atomic-layer deposition [34,35], reactive ballistic deposition [36], hydrothermal deposition [37–39], electrodeposition [40–46] and spray pyrolysis [47–49]. Spray pyrolysis stands out as one of the simplest large scale method for deposition of single phase $\alpha$-Fe$_2$O$_3$ photoanodes [50] and was therefore chosen as the sample preparation method for this study. We have to express that during this study we are aiming to investigate the influence of yttrium on hematite PEC performance and this is the other reason why we chose well applied spray pyrolysis method. To obtain hematite nanostructures for photoanodes, the vapour phase deposition has been suggested [51].

2. Experimental

2.1. Fabrication of $\alpha$-Fe$_2$O$_3$ and Y-doped $\alpha$-Fe$_2$O$_3$ thin films

Spray pyrolysis was used to produce Fe$_{2-x}$Y$_x$O$_3$ (x = 0, 0.05, 0.10, 0.2) thin films on FTO (fluorine-doped tin dioxide)-coated glass strips (2.5 × 1.2 × 0.4 cm); a detailed account of the method is given in our previous work [52]. Prior to deposition, the substrates were ultrasonically cleaned for 10 min in acetone, rinsed for 10 min in deionised water and dried at 120 °C for 20 min in air. Iron(III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, ≥ 99%) and Y(III) chloride hexahydrate ($\text{YCl}_3 \cdot 6\text{H}_2\text{O}$, 99.9%) obtained from Sigma Aldrich were dissolved in distilled water with a concentration of 0.1 M with the desired molar ratio. The FTO substrate was mounted on a hot plate preheated to 400 °C. Part of the FTO/glass strip was wrapped in aluminium foil to leave it uncoated for later electrical contacting for electrochemical measurements. The prepared solution was applied to the substrate via a pneumatic spray system (Star EVO-T mini, Taiwan) with a rate of 4 ml/min under a nitrogen pressure of 0.25 MPa using step-by-step mode of film growth. Spraying was performed in a sequence of 30 cycles of short spray pulses (0.5 s) followed by a 30-s pause to allow the temperature of the substrate to stabilise. After the deposition stage, thin film samples were annealed at 500 °C for 0.5 h.

2.2. Characterisation of thin films

A scanning electron microscope (SEM) (Tescan: model: Mira/Lmu, Czech Republic) in secondary electron mode with a 15 kV operating voltage was used for thin-film morphology characterisation. X-ray diffraction (XRD) patterns were recorded on a PANalytical XPert Pro powder diffractometer (Cu Kα, radiation).

Optical properties of un-doped and doped hematite thin films on a glass substrate were studied by using a UV–vis spectrophotometer (Shimadzu, UV-2450) to determine the absorption band edge and the band gap energy. The absorbance was measured by subtracting the absorbance of the glass substrate, which was taken as a reference in all measurements.

The X-ray photoelectron spectroscopy (XPS) and X-ray Absorption Spectroscopy (XAS) experiments were carried out at the D1011 beamline of the MAX-II synchrotron storage ring (Lund, Sweden). The beamline is equipped with a modified SX-700 plane grating monochromator. XPS spectra were measured using a Scienta SES-200 electron energy analyser in a fixed analyser transmission mode with 200 eV pass energy. The overall XPS resolution was 0.35 eV or better. The sample was positioned at normal emission (for XPS) with a 40° incident angle for the incoming photon beam. The binding energy scales for the XPS experiments were referenced to the binding energies of the C 1s (284.8 eV) photoemission line. The Fe 2p, Y 3d, C 1s and O 1s photoelectron spectral peaks were fitted by asymmetric Gaussian-Lorentzian line shapes after subtracting a Shirley background. The analysis was carried out using CasaXPS software (version 2.3.13) [53]. The XAS was measured in total electron yield (photocurrent) mode and the SX700 beamline monochromator resolution was set to 0.19 eV for the Fe 2p and 0.12 eV at the O 1s XAS.

2.3. Photoelectrochemical (PEC) measurements

Photoelectrochemical properties were measured in cells (Fig. 2) containing 1 M NaOH electrolyte with pH = 13, a platinum foil 12 cm$^2$ in size counter electrode (methyl cathode) and thin-film hematite sample deposited on a FTO/glass conductive substrate as a working electrode (1 cm$^2$, sealed with epoxy). A saturated calomel electrode (SCE) was used as a reference, assuming its potential +241 mV to normal hydrogen electrode potential. Open circuit potential was measured during 30 min in darkness; the photocurrent was measured using 20 s light pulses followed by 20 s darkness with a VoltaLab PGZ 301 potentiostat (Radiometer Analytical) measuring in parallel the volt-ampere (I-V) curves (potential is scanned from −100 mV to +500 mV with a speed of 2 mV/s). The photocurrent was calculated as the difference between the currents in the dark and under illumination, separately in each selected potential increment. After measurement of each sample the electrolyte solution was changed and the cell was rinsed with deionised water. LED light source with intensity 15 mW/cm$^2$ measured with 3A-P thermal sensor (spectral range 0.15–8 μ; OPHIR Photonics) was used for PEC measurements.
2.4. Mott–Schottky analysis

The fixed frequency (10 kHz) impedance measurements where performed in order to obtain the Mott–Schottky curves of the semi-conducting electrodes in the dark using a VoltaLab PGZ 301 (Radiometer Analytical) impedance analyser. Capacitance was measured for each sample at a frequency of 10 kHz while varying the sample bias from −500 to 0 mV in increments of 50 mV. The Mott–Schottky graph \( (1/C^2 \text{ versus electrode potential}) \) was plotted from the measured capacitance and using equation [54]:

\[
\frac{1}{C^2} = \frac{2}{e\varepsilon_0\varepsilon N} \left( V_{app} - V_{FB} - \frac{kT}{e} \right)
\]

where \( C \) is the capacitance of the barrier layer at the electrode/electrolyte interface, \( V_{app} \) is the applied bias potential, \( V_{FB} \) is the flat-band potential, \( N \) is the concentration of charge carriers in equilibrium, and \( T \) is the absolute temperature. The value of the flat-band potential \( V_{FB} \) is found by extrapolating the linear region in the Mott–Schottky plot to zero. From the slope of this linear region the concentration \( N \) of equilibrium charge carriers is estimated using the following equation:

\[
\text{Slope} = \frac{2}{e\varepsilon_0\varepsilon N}
\]

3. Results and discussions

Fig. 3(a) shows the X-ray diffraction patterns of the pure and Y-doped iron oxide thin films. The patterns indicate that the crystal structure in all the synthesised films is \( \alpha-Fe_2O_3 \) (JCPDS file no. 86-0050). Rietveld refinement was performed to obtain lattice constants of synthesised materials. Rietveld refinement show no yttrium related impurity phases, as well as hematite lattice constants increases with yttrium doping as demonstrated in Fig. 3(b), showing the yttrium incorporation, which in turn may produce contracted lattice contraction in close vicinity. Rietveld refinement also shows tiny amount of magnetite impurity phase in hematite sample, which diminishes with yttrium doping. Results indicate that yttrium stabilises spray pyrolysis derived hematite structure.

Fig. 4 shows SEM images for pristine \( \alpha-Fe_2O_3 \) and Y doped \( \alpha-Fe_2O_3 \) \((\alpha-Fe_{1-x}Y_xO_3)\) thin films. SEM analysis confirmed the presence of homogeneous densely packed (non-porous) solid oxide layers intimately attached to the substrate with a smooth surface and thickness below 500 nm. For all samples after annealing the film structure was formed from densely packed nano-sized grains without pores. We did not observe any differences in morphology between the samples in the SEM images.

XPS analysis was used to investigate the chemical state and the electronic structure of the Y-doped iron oxide thin films. Fig. 5(a) displays the Fe 2p photoelectron spectra of the undoped and doped \((x = 0.1 \text{ and } 0.2)\) samples, which show the two spin-orbit split Fe 2p
bands at 710.8 eV (2p3/2) and at 724.7 eV (2p1/2) and a weaker Fe3+
2p3/2 charge transfer satellite at 719.3 eV. The Fe 2p XPS of all these
samples gives a converging fit using a Fe3+ multiplet structure [54],
indicating that iron is consistently in the 3+ charge state. The Y 3d XPS
(Fig. 5(c)) with two partially resolved components at 157.3 eV (3d5/2)
and 159.4 eV (3d3/2) also identifies a Y3+ charge state [55,56].

The O 1s XPS (Fig. 5(b)) is measured at relatively low kinetic
energy, which corresponds to a very shallow probe depth of only a few
atomic layers, and therefore overrepresents the surface adsorbed spe-
cies, but also visualises the reactivity of the surface. The lowest binding
energy component (at 529.7 eV) corresponds to oxygen in the bulk
oxide lattice, whereas the two higher binding components correspond
to adsorbed hydroxylic (typically Fe(OH)3- and FeOOH-like species, at
531.3 eV) [57,58] and, further up, to surface adsorbed carboxylic

![Fig. 4. SEM micrographs of the pristine α-Fe2O3 ((a) and (c)) and α-Fe1.9Y0.1O3 ((b) and (d)) thin films.](image)

![Fig. 5. Photoelectron spectra of the Fe 2p (a), O 1s (b) and Y 3d (c) energy regions of the YxFe2-xO3 (x = 0, 0.1 and 0.2).](image)
oxygen species (532.7 eV) [59]. Although not fully resolved, the overall relatively large change upon doping visualises a tendency of favoured hydroxyl (and relatively decreasing carboxylic) oxygen adsorption at growing doping level, which can contribute to the overall increase of photoanode functionality, described further below.

An estimate of the relative abundancies in the surface region was made by comparing the XPS spectral band areas after removing a Shirley type background and normalising to the corresponding photo-absorption cross sections [60]. Although the absolute numbers should be taken with some caution (viz. given the shallow and somewhat varying probe depths at different edges) the signal ratios confirmed that the Y/Fe ratio increased according to synthesis specifications. For surface layer ~ 0.56 nm (imfp) at normalized to time, ring current, photoionisation cross section, and inelastic mean free path the observed compositions was Fe$_{1.8}$Y$_{0.2}$O$_3$ for Fe$_{1.8}$Y$_{0.2}$O$_3$ sample and Fe$_{1.78}$Y$_{0.22}$O$_3$ for Fe$_{1.8}$Y$_{0.2}$O$_3$ sample. The observed compositions are close to aimed compositions.

As a less critically surface sensitive probe, X-ray absorption (XAS) was used to further investigate the charge state and local symmetry information related to the (chemical element projected) partial densities of unoccupied states. The Fe 2p XAS (Fig. 6(a)) shows two peaks at approximately 710 eV and 723 eV, corresponding to the 2p$_{3/2}$-3d and the 2p$_{1/2}$-3d transitions, respectively. We note that the multiplet structures, which underlie the spectral distribution, are more clearly resolved in the XAS than XPS, because the XAS structures, which underlie the spectral distribution, are more clearly resolved in the XAS than XPS, because the XAS final state lies within the unoccupied density of states rather than in the continuum (as in XPS). Because the 2p$_{1/2}$-3d region suffers lifetime broadening from fast Coster-Kronig processes, we further consider the 2p$_{3/2}$-3d region around 710 eV. For the half-filled Fe$^{2+}$ 3d$^5$ high spin configuration (with the other spin band completely unoccupied), the main features of the multiplet can be rationalised within a more simple one-electron approximation, as a spectrum defined by the Fe 3d unoccupied band in the ground state. The crystal (ligand) field resulting from the octahedral oxygen coordination partly removes the degeneracy of the Fe 3d level and splits it into the triply degenerate t$_{2g}$ (directed in between the octahedral ligands) and the doubly degenerate e$_g$ states (directed towards the oxygen ligands), which give rise to the partly resolved peaks [57] as labelled in Fig. 6(a) for octahedral ligand field. Simulated spectra of both the octahedral (O$_h$) and tetrahedral (T$_d$) ligands, generated using the CTRMXAS software [62] are also provided in the figure to show that the former fits the data. It is significant here that this structure is not smeared out upon Y doping, which would happen if iron would start to form adjacent phases (i.e. yttrium iron garnet) and to take up the smaller tetrahedral voids (resulting in opposite and smaller splitting of the Fe 3d components), shown as a dashed line in Fig. 6(a) after incorporation of the larger Y ions, like for instance in yttrium iron garnet Y$_3$Fe$_2$O$_{12}$. As the spectrum immediately depends on the Fe site local symmetry (and even lattice parameters, via ligand field strength), the Y doping independent Fe 2p XAS indicates that Y is loaded into retained hematite lattice.

Given the invariance of the Fe 2p XAS, the moderate change of relative intensities at the leading edge of the O 1s XAS (Fig. 6(b), indicated with an arrow) is therefore more interesting, as it suggests dopant influence to increase the density of states near the bottom of the unoccupied band. The source of the change near the conduction band minimum is not trivial, since the main weight of the Y 4d states is commonly expected to be a few eV higher up [63-65], but it has been also observed earlier to vary rather widely in energy between different Y compounds (e.g. in Y$_2$O$_3$ vs. YFeO$_3$ [65], with even a similar minor change as we observe here at the leading edge of O 1s XAS for YFeO$_3$ as compared to hematite [65]) and with a significant covalent character of the bonds, with the formal charge state not achieved even in stoichiometric yttrium oxide [63]. The dopant related increase in the density of states near the bottom of the conduction band could facilitate the transport of visible light excited photoelectrons. When combined with the finding affinity to surface adsorb carboxylic species (as seen in O 1s XPS, above) and hence more surface sites more available for hydroxyl (and water), this could suggest a mechanism for the observed relatively high (visible) photocurrent values, despite reduced charge carrier density estimated from the Mott-Schottky plots (below).

The optical absorption spectra of different samples are shown in Fig. 7. The absorption edge of a material is related to the character of the transitions across the band gap. According to the Davis-Mott and Tauc models, the optical absorption edge in the high absorption coefficient region (above $10^4$ cm$^{-1}$) of amorphous and nano-crystalline semiconductors follows the characteristic weight function [66,67]:

$$
(\alpha \cdot h\nu)^2 = B \cdot (h\nu - E_g)
$$

(5)

where $\alpha$ – absorption coefficient, $h\nu$ – the energy of incident light in electron volts (eV), $B$ is a constant, $E_g$ is optical band gap or absorption edge, $n$ is an exponent with values 1/2, 3/2, 2 and 3 depending on the type of the electronic transition at the absorption edge. For an allowed direct transition, the $n$ will have a value of 1/2, and for an allowed indirect transition, the $n$ will have a value of 2 [67].

The strong absorption band close to the band gap edge in hematite is due to indirect Fe d–d transitions between the ligand field split Fe 3d orbitals [68], therefore the band-gap energy of the thin films was estimated from a plot of $(\alpha \cdot h\nu)^{1/2}$ vs $h\nu$ (eV), where $\alpha$ is the absorption coefficient and $h\nu$ is the photon energy in eV, as an intercept of the energy axis with a tangential straight line of the linear part of the graphs (Fig. 5(b)). The values estimated from the figure for the indirect optical band-gap energy for the un-doped hematite is 1.84 eV, while for the Y-doped hematite samples it decreases to 1.75 eV (Fe$_{1.9}$Y$_{0.1}$O$_3$) and 1.7 eV (Fe$_{1.8}$Y$_{0.2}$O$_3$), which qualitatively agree with an earlier theoretical estimate [69]. The experimental band gap values reported for hematite is in range from 1.9 to 2.3 eV depending from point defects.

![Fig. 6. The Fe 2p (a) and the O 1s total electron yield X-ray absorption spectra (b) of the Y$_x$Fe$_{2-x}$O$_3$ (x = 0, 0.1 and 0.2). The $t_{2g}$, $e_g$ labels refer to splitting under octahedral ligand field. A simulated Fe 2p XAS is produced using the CTRMXAS package [55] for octahedral ligand field 10Dq = 1.3 eV. A corresponding tetrahedral site simulation is given to illustrate the absence of this component in the experimental data.](image-url)
The small deviation for pristine hematite in our case could be related to magnetite impurity phase.

Measurements of the volt-ampere curve with pulsating light source indicate an increase of photocurrent at increased bias against SCE, which confirms n-type conductivity (Fig. 8(a)) for all the synthesised un-doped and Y-doped hematite thin films. Photoelectrochemical performance of thin films is higher when Fe$^{3+}$ is substituted by Y$^{3+}$ in the hematite lattice (Fig. 8(b)). The photocurrent reached a maximum when Y concentration was $x = 0.1$ (Y$_x$Fe$_{2-x}$O$_3$), thus it seems that it is the optimal concentration, above which the observed photocurrent decreases. The decrease in the photocurrent beyond a certain doping level can be attributed to the fact that higher concentrations of dopant...
provide more defect-scattering/recombination pathways [70]. At the smaller doping levels defect-scattering/recombination is not absent and doping-scattering goes alongside to each other, which is the reason for optimum doping level where positive input from doping is larger than negative.

To understand the effect of Y incorporation on charge transport, values of flat-band potential were experimentally determined by measuring the capacitance at the photoelectrode/electrolyte junction for varying electrode potential according to the Mott–Schottky theory [56]. All the measured films exhibited positive slopes in Mott–Schottky plots (Fig. 9(a)), consistent with the n-type conductivity. The flat-band potential estimated from the Mott–Schottky plots are shown in Fig. 9(b). As it can be seen from the figure, by increasing the Y concentration the flat-band potential shifts to the negative (cathodic) potential side from −814 mV SCE (Fe2O3) to −1171 mV SCE (Y0.2Fe1.8O3). The flat band potential values are similar to those reported by Shinde et. al [22]. More negative values of the flat-band potential indicate more effective separation of the photoinduced charge carriers and energy level shifting to a better position against water redox potential.

Finally, the stability under PEC measurements for the most active Fe1.9Y0.1O3 sample was studied. As demonstrated in Fig. 10, sample shown no visible degradation in performance in 5 h during PEC measurement. There were also no changes in crystalline structure observed after 5 h PEC measurement as demonstrated in Fig. 10(b).

4. Conclusions

In summary, Y-doped hematite thin films (YxFe2-xO3) were deposited via a spray pyrolysis method using aqueous solutions of metal chlorides. SEM studies revealed that all thin film samples completely covered the substrate and layers had a closely-packed grain structure, flat surface and thickness below 500 nm. XRD measurements showed a single-phase hematite structure, while XPS and XAS studies confirmed formation of yttrium doped hematite. We observe enhanced photoelectrochemical performance of the hematite thin films when substituting Fe3+ with Y3+ in the hematite lattice. The photocurrent attained a maximum when the concentration of Y was x = 0.1 (YFe2O3). An analysis of the Mott–Schottky plots suggests that an increase of the concentration of Y shifts the flat-band potential in the cathodic direction, thus having a positive impact on photo-electrochemical performance.

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