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Photo-Electrochemical Solar-to-Fuel Energy Conversion by Hematite-Based Photo-Anodes – The Role of 1D Nanostructuring

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Abstract: Photo-electrochemical (PEC) water splitting (WS) using metal oxide semiconductors is regarded as a promising approach for the renewable production of fuels and energy vectors such as hydrogen (H_2). Among metal oxide semiconductors, iron oxide in the form of hematite ($\alpha\text{-Fe}_2\text{O}_3$) is one of the most researched photo-anode materials, mainly due to its ability to absorb photons up to 600 nm combined to a set of desirable properties such as high photo-corrosion resistance, environmental friendliness, large abundance and relatively low production costs. However, hematite main disadvantages are a low electrical conductivity and a high rate of charge recombination; both these shortcomings drastically limit functionality and efficiency of hematite-based photo-anodes in PEC devices. One-dimensional (1D) nanostructuring is a powerful tool to tackle such disadvantages as it provides the photoelectrode material with increased surface area along with directional charge transport properties and short charge diffusion distances to the electrolyte – these features can improve the lifetime of photo-generated charges and/or enhance the charge transfer efficiency, and can consequently lead to a superior photo-electrochemical performance. At the same time, chemical/physical modification can also compensate natural weaknesses of hematite in water photoelectrolysis. The present mini-review outlines a series of most effective strategies for the fabrication of 1D hematite nanostructures as well as for their physicochemical modification, mainly by doping or co-catalyst decoration, to achieve superior PEC activity.

Keywords: Hematite; Photoanode; photoelectrochemistry; semiconductors.

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1 Introduction

1.1 Water splitting by semiconductors

Fossil fuels are the main source of global energy. The energy production by fossil fuels is typically achieved by combustion, which results in major production of CO₂ and subsequent global warming. Hydrogen (H₂) is one of the most promising alternative fuels not only due to its high energy density but also because in principle it can be produced from water (an abundant source), and since its combustion to liberate energy leads only to innocuous water as reaction product. Thus, while the industrial scale production of hydrogen is still based on reforming of methane [1], huge research efforts are devoted to find a cost effective method for H₂ production through water splitting.

The following reactions represent water:

The overall reaction shows a Gibbs free energy $\Delta_r G^0 = 273.2 \text{ kJ/mol}$. Therefore, this is not a spontaneous reaction. One of the most promising solutions is using semiconductor materials as photoelectrodes that under light illumination can convert H₂O into H₂ and O₂. Ideally, the ultimate goal of this approach is to transform solar light into clean energy (fuels or chemicals) in a cost effective way.

In a conventional PEC device, photons with adequate energy ($h\nu \geq \text{band-gap}$, E_g) are able to generate excited charge carriers with enough energy to overcome the activation energy for water splitting. Relevant stages in photo-electrochemical water splitting are: light absorption, separation of charge carriers, charges transport holes (h_{VB}^+) towards the photoelectrode surface and electrons (e_{CB}^-) to the back contact, and surface reactions (see Figure 1a).

In general, essential necessities for photoelectrodes are a low production cost, high chemical stability, high charge conductivity, low recombination rate of generated charges, and rapid charge transfer at the solid/liquid interface. Additionally, the photoelectrode material should have a conduction band position more negative than the redox potential of H₂ evolution reaction and a valence band position more positive than the redox potential of O₂ evolution reaction from water (in a photoelectrochemical device a slight deviation from the mentioned

Fig. 1: (a) Structure of a photoelectrochemical cell based on an n-type semiconductor; (b) Band gap and corresponding edge positions of semiconductors in contact with an aqueous electrolyte at pH = 0.

rule to a certain extent can be recovered by applying bias voltage). Clearly, in view of utilizing sunlight to drive PEC water splitting, it is a strict requirement that the semiconductor absorbs a significant portion of visible light, i.e. to be able to efficiently convert sunlight to hydrogen and oxygen.

Band edges and band gap energies of most common semiconductors are reported in Figure 1b. So far, several semiconductors were explored for photoelectrochemical water splitting such as Si, Ge, SiC, CdSe and, etc. [2]; however, these semiconductors generally suffer from severe photocorrosion and from chemical instability in aqueous electrolytes; on the contrary, photoelectrodes based on transition metal oxides such as hematite can provide a proper band gap positioning for oxygen evolution reaction (OER) and hydrogen evolution reaction (HER) reactions together with appropriate chemical and photo-electrochemical stability.

1.2 Solar-to-hydrogen (STH) conversion efficiency

The assessment of the photoconversion efficiency achieved by different semiconductor materials needs that the photoelectrode performance is measured under illumination with a standard solar spectrum, i.e. usually the AM 1.5 solar spectrum at a given power density (100 mW cm^{-2}). This condition can be achieved with real sunlight only at specific places on earth and in specific periods of the year (with dependence on weather variability). Therefore, the photoelectrochemical efficiency is mostly measured under irradiation with artificial light sources. This approach is comparably more convenient than using sunlight

illumination because artificial sources (commonly called “solar simulators”) can provide a stable irradiation power density and their intensity is constant with time.

For the advancement of Photoelectrochemical (PEC) watersplitting (WS) technologies, reliable identification protocols for photoelectrode materials and standards to compare semiconductors with one another are essential. Thus, parameters that define the performance of a PEC device under solar irradiation, the solar-to-hydrogen (STH) conversion efficiency can be regarded as a most practical parameter for reporting the efficiency of photoelectrochemical device.

The STH conversion efficiency depicts the total efficiency of a PEC WS device subjected to an AM 1.5 G illumination [3]. Thus, in other words, STH can be seen as the ratio of chemical energy stored in the form of hydrogen molecules to the solar energy input, and can be calculated by (4):

$$\text{STH} = \left[\frac{r_{\text{H}_2} \times \Delta G}{P_{\text{in}} \times A} \right]_{\text{AM 1.5 G}} \quad (4)$$

where r_{H_2} is the hydrogen production rate ($\text{mmol}_{\text{H}_2} \text{ s}^{-1}$), ΔG is the difference in Gibbs free energy per mole of H_2 produced (237 kJ/mol), P_{in} is the incident illumination power density (mW cm^{-2}) and A is the exposed electrode area (cm^2). STH can also be calculated as a function of the short-circuit photocurrent density, j_{SC} (6) [4]:

$$\text{STH} = \left[\frac{j_{\text{SC}} \times 1.23 \text{ V} \times \eta_{\text{F}}}{P_{\text{in}}} \right]_{\text{AM 1.5 G}} \quad (5)$$

where 1.23 V is the thermodynamic water splitting potential and η_{F} the Faradaic efficiency for H_2 generation. It should be stressed that (4) and (5) are valid only if measurements are accomplished under AM 1.5 G illumination and in the absence of rival redox couples and sacrificial molecules in the electrolyte (e.g. electron donors or acceptors).

1.3 Hematite-based photoanodes

Among all considered metal oxide semiconductors for photoelectrochemical applications, hematite has attracted a significant research interest because of its earth abundance, chemical and photoelectrochemical stability, being an eco-friendly material and having low production costs [5–9]. Hematite absorbs light in the visible range up to 600 nm due to its optical bandgap of ~ 2.1 eV. This implies

the absorption of ca. 40% of solar spectrum [10]. Despite the mentioned advantages, the conduction band edge of hematite is more positive than the hydrogen evolution reaction (HER) potential. Accordingly, an external electrical bias is needed to promote hydrogen evolution; in other words, H_2 evolution does not occur on hematite under open circuit conditions [7]. Nonetheless, the valence band (VB) of hematite lies at more positive potential than the electrochemical potential required to form O_2 from H_2O [$E^\circ(O_2/H_2O)$] – that is, holes in hematite are able to oxidize water to oxygen gas [7].

Additionally, hematite suffers from a characteristically low electrical conductivity, low electron-hole lifetime (less than 10 ps) and a short hole diffusion distance (5 nm), which drastically decrease the efficiency of hole transfer at the semiconductor/liquid junction [9, 11]. All these features are usually regarded as the major constraints in PEC water splitting performance for hematite photoanodes [10, 12].

Several physicochemical modification approaches have been explored for hematite-based photoanodes, aiming at overcoming the above-mentioned intrinsic limitations. Common strategies are: (I) doping, that is, the embedment of other elements into the semiconductor lattice, to adjust the semiconductor's electronic properties like the donor density (in lower doping concentration) and the band gap (in higher doping concentration) and: (II) co-catalyst decoration, to improve charge carrier separation (charge “extraction” from the semiconductor) and charge transfer at solid/liquid interface; (III) photo-sensitization, e.g. by surface modification with plasmonic materials, quantum dots, or organic dyes to increase visible light absorption; and (IV) surface passivation, i.e. the deposition of thin overlayers to limit charge trapping, avoid surface charge recombination, and improve charge transfer to the environment.

Ultimately, another practical strategy is the nanostructuring of the photo-electrode material into nanoparticles, nanotubes, nanoplatelets, etc. This is an efficient approach in the context of heterogeneous (i.e. solid-liquid and solid-gas) reactions since it typically leads to a large surface-to-volume ratio for the semiconductor (large surface area) that can facilitate charge transfer at the semiconductor/environment interface. Also, e.g. for one-dimensional nanostructures (discussed below), their geometry is crucial for achieving a high photoelectrochemical water splitting efficiency owing to the control over light absorption and due to orthogonal charge separation effects, as well as for establishing preferential charge percolation pathways.

Herein, we provide an overview of most common synthesis strategies of one-dimensional (1D) hematite nanostructures and their use as photoanodes for photo-electrochemical water splitting. In this context, we also discuss briefly the most relevant strategies for doping and surface decoration.

2 Nanostructuring for PEC water splitting

Nanostructured materials are able to offer considerably altered physical and chemical properties, and can consequently exhibit exclusive functionalities [13–16]. In general, the terminology “nanomaterial” is used to indicate a material single unit with size (in at least one dimension) below 100 nm [17]. Based on this definition, the typical structural features of zero- (0D), one- (1D), two- (2D), and three-dimensional (3D) nanomaterials can be visualized as sketched in Figure 2 [18–23].

Several typical features of nanomaterials are beneficial for PEC applications, e.g.: (i) directional light absorption and enhanced charge-carrier separation/collection (charge separation can be further improved by an internal electric field); (ii) tunable exposure of specific crystal facets, to adjust flat band potential, band-bending, surface states, etc.; (iii) large surface area that, in stark contrast to bulk materials, provides a great advantage when a material is intended for catalytic applications (i.e. high number of active surface spots to enable adsorption of reactants, and large interfacial contact with the reaction environment that can lead to higher reaction rates).

Particularly hierarchical nanostructures, regarded as 3D-nanomaterials, are gaining increasingly larger attention for photoelectrochemical water splitting applications. In general, a hierarchical nanostructure is composed of e.g. arrays of individual “support” units (such as an assembly of oriented 1D nanostructures) onto which nanodimensional building blocks are grown – these typically include nanoparticles (0D), nanowires/rods/tubes (1D) and nanosheets (2D). Therefore, hierarchical nanostructures often look like “branched” architectures that concurrently unite the properties of the one-dimensional backbone (e.g. enhanced carrier separation and directional charge transport) with a considerably increased surface area and a much higher amount of active sites, because of the highly porous assembly provided by the attached nanosized subunits [24–26]. In most

Fig. 2: Classification of different nanostructures based on their nanoscale dimensions.

cases, hierarchical nanostructures can be produced by combining or adapting established processes for nanostructure synthesis: e.g. chemical solution synthesis, chemical vapor deposition, hydrothermal synthesis, or photodeposition [27–29].

Regardless of the adoption of a sole or various synthesis methods, hierarchical nanostructures can be composed of either a single material (Figure 3a–d) or a mixture of two or more (Figure 3e–h) [35]. In the former case, a hierarchical nanostructure is mainly exploited in view of its notably higher surface area – a straightforward example and key function is as photo-anode in a dye-sensitized solar cell [32]. Hierarchical nanostructure made of two or more materials can provide additional benefits, which is, the probability of combining materials with different assets and band structures, e.g. to construct heterojunctions. This in turns can be utilized to improve either the electron collection from the branched-material to the back-bone nanostructure, the hole transfer to the electrolyte and/or visible light absorption.

Fig. 3: (a) Top view and cross-sectional (inset) SEM images of a 3D dendritic hematite and (b) high magnification SEM image of distinct 3D dendritic hematite. (c) Cross-sectional SEM image of 3D hierarchically branched hematite nanorods; (d) high magnification image of distinct hierarchically branched hematite nanorod. (e) Cross-sectional SEM image of $\text{WO}_3\text{-Fe}_2\text{O}_3$ film. The dotted white line indicates the FTO/ $\text{WO}_3\text{-Fe}_2\text{O}_3$ film interface (f) high magnification FESEM image of SnO_2 nanowire coated with TiO_2 nano needle leaf-structures. (g,h) SEM images of a TiO_2 nanotree heterostructure—scale bars are $1\ \mu\text{m}$. Fig. (a,b) are reproduced from Ref. [30] with permission from the John Wiley & Sons. Fig. (c,d) is reproduced from Ref. [31] with permission from the Royal Society of Chemistry. Fig. (e) is reproduced from Ref. [32] with permission from the American Chemical Society. Fig. (f) is reproduced from Ref. with permission from the Elsevier [33]. Fig. (g,h) are reproduced from Ref. [34] with permission from the American Chemical Society.

3 1D hematite synthesis and PEC WS applications

In the following section, we deal with various one-dimensional assemblies of hematite normally applied for PEC WS experiments. We mainly focus on 1D-nanostructures like nanowires, nanorods, and nanotubes (NTs).

3.1 Formation of 1D hematite

Solution-based growth methods, such as hydrothermal synthesis, present a series of advantages including good scalability, simple handling, and low production costs. In spite of the numerous morphologies that can be formed via solution-based methods (nanoparticles of various shape and size, nanorods, nanotubes, nanowires, nanoflowers, etc.), other methods like self-organizing anodization and template-assisted synthesis have however also been developed.

3.1.1 Hydrothermal methods

Hydrothermal synthesis is a most frequently used approach for the fabrication of nanorods/wires/tubes of various metal oxides on a proper back contact substrate. For hematite, normally, iron(III) chloride is used as precursor [36–40]. Hydrothermal synthesis is accomplished in a pressure container, in aqueous or organic-based solutions [41]. Solution volume and temperature largely influence the internal pressure; these parameters along with the nature of the capping agent provide means to control the resulting hematite morphology in the form of nanorods, nanowires and nanotubes [42]. Hydrothermal hematite nanotubes can be produced from FeCl_3 solutions in the presence of $\text{NH}_4\text{H}_2\text{PO}_4$ at 220 °C [43–45]. Regardless of the precursors, the resulting nanotubes are single-crystalline in nature and feature tube lengths in the 200 nm – 1 μm range, with a diameter in the 100–150 nm range and a wall thickness of 25–30 nm [43–46].

3.1.2 Self-ordering anodization

In general, hydrothermal processes lead to loose agglomerates of tubes dispersed in a solution with non-homogeneous tube size (e.g. length and diameter). However, as mentioned above, a well back-contacted photoelectrode material is crucial to exploit orthogonal charge separation and directional charge transport properties of 1D nanostructures.

In this context, electrochemical anodization offers a most straightforward way to fabricate directly back-contacted layers of vertically oriented one-dimensional hematite nanostructures for PES WS applications. Additional

key advantages of self-ordering anodization are the scalability, the fine control at the nanoscale over the photoanode morphology, and the versatility i.e. it can be used to grow nanostructures of various metal oxides (Figure 4a,b) [47, 52, 53].

Electrochemical anodization is typically accomplished in a 2-electrode electrochemical setup where a metal substrate is immersed in a suitable electrolyte and exposed to a positive electrical bias. During the earlier stage of anodization, a metal oxide starts growing at the anode surface (the electrode with positive bias) in the form of a compact oxide. The growth is ascribed to (inward and outward) ion-migration at the anode/electrolyte interface. Precisely, metal cation migrate outward (substrate to electrolyte), while O^{2-} ions from the electrolyte migrate in the opposite direction (Figure 4c). In most common diluted electrolyte (e.g. H_2SO_4 , HNO_3) this process is self-limited as the formed anodic oxide is stable in the anodizing electrolyte and while such oxide layer thickens, the electric field gradually drops until ion migration consequently ceases. This results in the formation of compact oxide film, which does not reveal particular morphological topographies.

Nonetheless, when using electrolytes containing solvatizing anions e.g. fluoride (F^-) ions in a suitable concentration, the formed anodic oxide becomes partially soluble in the anodizing medium and a steady-state equilibrium can be established between the electrochemical oxide formation and its dissolution rate that leads to the growth of porous layers of e.g. nanotube, nanopore or nanochannel arrays (Figure 4c). Anodization parameters play a crucial role in determining the degree of self-ordering of such one-dimensional nanostructures

Fig. 4: (a) Classic 2-electrode electrochemical anodization set-up and typical anodic structures formed from different valve metals. (b) Some example of valve metal oxide nanotube fabricated by anodization. (c) High field oxide formation in the presence of fluoride ions in the anodizing medium. Fig. a is reproduced from Ref. [47] with permission from the Royal Society of Chemistry. Fig. b-Ti is reproduced from Ref. [48] with permission from the Royal Society of Chemistry; inset is reproduced with permission from Ref. [49] with permission from the American Chemical Society. Fig. b-W is reproduced from Ref. [50] with permission from the American Chemical Society. Fig b-Ta is reproduced from Ref. [51] with permission from the Elsevier. Fig. c reproduced from Ref. [47] with permission from the Royal Society of Chemistry.

as well as their morphological features. Diverse experimental conditions result in optimal morphologies for different metals [52–55]. As anodic Fe oxide nanotube layers are normally amorphous, to convert them to hematite a thermal treatment in a range of temperatures from 400 to 700 °C is essential [53, 55].

3.2 Physicochemical modifications of 1D hematite

Fe oxide may crystallize in various crystalline structures (and stoichiometries) such as α , β , γ , ϵ phases. In particular, α -Fe₂O₃, i.e. hematite, is the most thermodynamically stable polymorph of iron oxide under ambient conditions. It has a rhombohedral lattice system, with lattice parameters $a = 5.0356$ Å and $c = 13.7489$ Å [56]. Understanding the band gap and the position of conduction and valence edges is necessary to evaluate the performance of the material for solar energy conversion [57]. Hematite absorbs photon below its optical band gap $E_g \sim 2.1$ eV in the visible-near infrared region, which is generally proposed that this is probably ascribed to spin-forbidden d-d transitions associated to Fe³⁺ ions [58].

Hardee and Bard reported on the use of hematite as a photo-anode material for water splitting for the first time. For hematite thin films deposited by chemical vapor deposition on Ti or Pt foils they observed a photocurrent onset at $\lambda = 550$ nm [6] (under 0.8 V vs. SCE in a KCl-based electrolyte). Sanchez et al. reported a 40% efficiency for water splitting on Nb-doped (1.5 mol%) hematite single crystals at 370 nm at +0.5 V vs. SCE [59, 60]. IPCE results up to 60–80% in the 300–400 nm range were reported for Pt decorated single-crystalline hematite nanostructures.

The above studies reached the conclusion that hematite cannot spontaneously reduce water to H₂ and an external bias is crucial for the water splitting reaction. There are also some other factors that limit the solar energy conversion performance of hematite and need to be considered to design efficient hematite photoanodes, namely the slow water oxidation reaction (OER) kinetics, a low light absorption coefficient, and the short solid-state diffusion length of holes.

The two main factors causing the low OER kinetics are (i) the presence of surface oxygen vacancies and crystalline disorder, and (ii) an increased valence band Fe³⁺ character which increase the mismatch in d orbitals and subsequently make the charge transfer slow [9, 61]. To tackle the crystalline disorder, hematite can be decorated by thin surface passivation layers that reduce surface defects (h⁺ trapping) and limit hole back injection [62–66].

Several studies were carried out to optimize the morphology of hematite photoelectrodes by nanostructuring, in order to address the intrinsic low absorption coefficient and short hole diffusion length of hematite.

3.2.1 Doping and conductivity enhancement

Severe losses in energy conversion ability are in the case of hematite due to a low mobility of electrons, which consequently leads to electron-hole recombination. Doping hematite, with either n- or p-type dopants, can overcome such a limitation [67–69].

It has been reported that Ti-doped hematite with a coral-like morphology shows a high PEC performance compared to undoped counterparts owing to a synergistic effect between the high specific area (significantly larger than that of the reference undoped material) and the increased donor density resulting from Ti doping and oxygen vacancies (Figure 5a,b) [70]. The amount of doping is a crucial factor that needs to be optimized in order to achieve the desired effect.

Thermally-induced diffusion of Sn from the FTO substrate is a simple approach for doping hematite. Sivula et al. [8] reported that an enhanced

Fig. 5: (a) Linear sweep voltammetry scans of reduced and Ti-doped hematite nanoarrays in light and dark condition. (b) SEM images and TEM elemental mapping of Ti-doped hematite nanorods. (c) Effects of low (left) and high (right) Nb doping amounts on hematite morphology and properties. (d) Schematic representation of thermally induced Sn-doping of α -Fe₂O₃ nanorod arrays and corresponding photoanode performance, content of diffused Sn and FTO resistivity change as a function of the annealing time. Fig. a,b is reproduced from Ref. [70] with permission from the Royal Society of Chemistry. Fig. c is reproduced from Ref. [71] with permission from the permission from John Wiley & Sons. Fig. d is reproduced from Ref. [72] with permission from the American Chemical Society.

photocurrent of hematite layers on FTO can be ascribed to the enhancement of the optical absorption coefficient, due to the structural distortion of the hematite lattice induced by unintentional tin-doping. A report by Ling et al. [73] ascribed the enhanced PEC performance of Sn-doped hematite to an increased donor density (i.e. $5.38 \times 10^{19} \text{ cm}^{-3}$ compared to $1.89 \times 10^{19} \text{ cm}^{-3}$ for hematite) and hence to a higher carrier conductivity. As a result it should be noted that Sn is able to influence both optical and electrical properties of hematite.

Sn-doping, however, presents some drawbacks when achieved by high temperature annealing: by annealing at 800 °C significant undesired changes in hematite occurred too, namely in its stoichiometry. A 10 min annealing was though reported to be optimal to achieve an increase in conductivity without any clear detrimental alteration of the material (Figure 5d) [72]. Another side effect of high temperature treatment is a possible destruction of the nanoscale morphology of hematite. Clearly, both effects (stoichiometry variation and nanostructure loss) have a negative influence on the overall PEC performance.

As an alternative to high temperature treatments, Lee et al. and Chitrada et al. reported on Si-doped hematite nanotube layers [74, 75] formed by anodizing Fe–Si alloys with various Si contents; this approach allows for a direct formation of iron oxide NT arrays with incorporated Si doses.

Doping hematite by a single dopant into the oxide lattice may introduce some undesired side effects, such as the narrowing of the space charge layer and/or the generation of recombination centers. A reasonable combination of two (or more) dopants can however be vital to avoid such disadvantages. This is the case of Sn^{4+} and Be^{2+} co-doped hematite 1D nanostructures. For example, although Sn^{4+} can provide enhanced conductivity, its presence in the hematite lattice as sole dopant leads to shallow n-type defect states beneath the conduction band that in turn cause an undesired band edge shift and increase micro-strain in the hematite lattice, reducing the Fe–O bond ordering. On the contrary, the co-presence of Be^{2+} ions attenuates these negative effects, by improving hematite conduction band and recovering hematite lattice distortion. For the optimized sample a maximum photocurrent density of 1.7 mA cm^{-2} at 1.23 V vs. RHE has been reported [76]. Similar results have been reported also for other co-doped systems such as Ti–Sn [77] and Ti–Si [78].

3.2.2 Co-catalyst decoration

A most effective method to accelerate the hole transfer step and thereby accelerate the oxygen evolution reaction (OER) at the photo-anode surface is by the modification of hematite with an oxygen evolution catalyst (OEC). It has been shown that non-stoichiometric IrO_x nanoparticles on hematite can decrease the

overpotential for the water oxidation reaction to an even larger extent [79] than IrO_2 . In another study it was demonstrated that that approximately 2 nm in diameter IrO_2 nanoparticles on hematite nanostructured photo-anodes can lead to a 200 mV cathodic shift in the onset potential and rise the photocurrent from 3.45 to 3.75 mA cm^{-2} [80]. However, in spite of the evident beneficial effects on hematite performance, the high cost of Ir significantly limits its practical application to PEC WS devices, and a great deal of work has been carried out to identify earth abundant, noble metal-free OER co-catalysts.

Examples of efficient, non-noble co-catalyst materials for hematite photo-electrodes are cobalt-phosphate, FeOOH , Ni-Fe , NiOOH , and Zn-Co based layered double hydroxides (LDHs). The functionality of cobalt-phosphate based co-catalysts lies in the bridging effect of phosphate ions that facilitates hole injection from hematite to Co ions – Co-Pi , for example, is a most effective co-catalyst on hematite nanostructures and was shown to be able to markedly improve the overall photoanode current density and to shift the current onset potential to more negative values [62, 63, 81].

It was more recently shown that FeOOH , NiOOH , and Zn-Co and Ni-Fe LDHs can exhibit extraordinary performance when used in combination with hematite in photo-electrochemical devices [65, 66, 82]. Common methods to deposit oxy-hydroxide and LDH layers onto hematite nanostructures are based on solvothermal techniques, electrodeposition or photoelectrodeposition, and pulsed laser deposition (PLD) [83–86]. For all these co-catalyst/hematite combinations, a notable rise in photocurrent along with a drop in water oxidation overpotential has been reported compared to pristine hematite photoelectrodes.

4 Conclusions

Research in the last decades has brought hematite in the spotlight as promising candidate to fabricate photoanodes for photoelectrochemical water splitting. A first reason is that compared to more classic semiconductor materials (Si , CdS , CdSe , GaAs , etc.), hematite is not only substantially more chemically stable against (photo)corrosion in a wide range of (electro)chemical conditions, but is also much cheaper, and more abundant on earth, easy to synthesize and nanostructure, and eco-friendly. In addition, compared to the most investigated, photocorrosion-stable metal oxide semiconductor counterpart, i.e. TiO_2 , hematite features more desirable light absorption properties as it can harvest a much wider portion of the solar spectrum.

Despite these positive aspects, still some peculiar drawbacks hamper the efficiency hematite based PEC devices and their development for real-life

applications. A main issue is certainly the limited charge transfer kinetics intrinsic to the oxide.

In this mini-review, we have shown that a potential solution to overcome charge transfer limitations of hematite in PEC arrangements is one-dimensional nanostructuring. Not only can 1D nanostructuring provide a photoelectrode with high surface area (a prerequisite for efficient heterogeneous reactions) but in general for hematite photoanodes it can enable also superior charge transport and transfer properties through orthogonal charge separation, by providing directional charge (electron) percolation pathways and short diffusion distances for holes towards the semiconductor/electrolyte interface. In addition, 1D nanostructures are a versatile platform for the construction of 3D structure, hierarchical heterojunctions, thereby providing further advantages such as enhanced light absorption and charge separation properties.

A range of fabrication methods and inherent advantages and disadvantages were discussed. Mainly, we focused on most promising synthesis pathways, namely solvothermal techniques and self-ordering electrochemical anodization. Particularly in the context of self-ordering anodization, we outlined how highly-ordered 1D oxide geometries can be easily fabricated, not only for hematite but also for a large palette of different semiconductor metal oxides. Main advantages of such 1D anodic hematite structures (and in general of 1D anodic oxides) are the ease of fabrication and the large degree of morphological control (nanotube length, wall thickness, tube diameter). Moreover, these structures can be directly grown on conductive metal substrate, i.e. are well back-contacted and can be straightforwardly used for (photo)electrochemical applications. We discussed in addition means to improve further the photoelectrochemical water splitting performance by tuning the physicochemical features of hematite photoelectrodes, such as by doping, band gap engineering and co-catalyst decoration strategies.

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