

Review

Surface Modification of Hematite Photoanodes for Improvement of Photoelectrochemical Performance

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Abstract: Solar water splitting is a promising method for producing renewable fuels. Thermodynamically, the overall water splitting reaction is an uphill reaction involving a multiple electron transfer process. The oxygen evolution reaction (OER) has been identified as the bottleneck process. Hematite (α -Fe₂O₃) is one of the best photoanode material candidates due to its band gap properties and stability in aqueous solution. However, the reported efficiencies of hematite are notoriously lower than the theoretically predicted value mainly due to poor charge transfer and separation ability, short hole diffusion length as well as slow water oxidation kinetics. In this Review Article, several emerging surface modification strategies to reduce the oxygen evolution overpotential and thus to enhance the water oxidation reaction kinetics will be presented. These strategies include co-catalysts loading, photoabsorption enhancing (surface plasmonic metal and rare earth metal decoration), surface passivation layer deposition, surface chemical etching and surface doping. These methods are found to reduce charge recombination happening at surface trapping states, promote charge separation and diffusion, and accelerate water oxidation kinetics. The detailed surface modification methods, surface layer materials, the photoelectrochemical (PEC) performances including photocurrent and onset potential shift as well as the related proposed mechanisms will be reviewed.

Keywords: hematite; photoelectrochemical; water oxidation; surface modification; flatband potential; onset potential; photocurrent; kinetics; photoanode

1. Introduction

Solar water splitting is a technology that can potentially produce a clean, environmentally friendly and cheap hydrogen fuel by using renewable energy sources. It allows to collect and store solar energy in chemical bonds and thus to overcome the challenge of daily and seasonal variability in renewable energy [1]. However, even though the electrolysis of water is considered to be one of the easiest methods to obtain hydrogen [2], the required high overpotentials still hinder a large scale application. Thermodynamically, the overall water splitting reaction is an uphill reaction ($\Delta G = 237$ kJ/mol) involving a multiple electron transfer process [3]. The oxygen evolution reaction (OER) has been identified as the bottleneck for the conversion process because of its large requisite overpotential [4]. Hematite (α -Fe₂O₃) is predicted to be an efficient photoelectrode material due to its moderate band gap ($E_g = \sim 1.9$ – 2.2 eV), chemical stability, abundance, non-toxicity and low cost [5–7]. A photocurrent of 12.5 mA cm⁻² under AM1.5 solar light irradiation is predicted [8]. Although a respectable photocurrent onset potential (V_{onset}) of <0.8 V vs. reverse hydrogen electrode (RHE) and photocurrents of 3.2 mA cm⁻² under AM1.5 solar light irradiation have been achieved [9], the reported efficiencies are notoriously lower than the theoretical value. It is worth mentioning that the V_{onset} is the shift or deviation from the flatband potential (V_{fb}). The flatband potential (V_{fb}) is the potential

required to bring back the semiconductor band edges to their flat band position from the bending position at the hematite/electrolyte junction. V_{fb} is an intrinsic property of hematite and one of the key parameters used in the evaluation of the photocatalytic activity of the photoelectrode and mainly affects the probability of charge recombination. The V_{fb} of hematite is around 0.4 V vs. RHE [9]. The quantity $V_{onset} - V_{fb}$ is generally referred to as overpotential for the solar water oxidation. Thus, a smaller value for $(V_{onset} - V_{fb})$ indicates a lower external bias (overpotential) required and hence implies a better photocatalytic activity. The poor performance of hematite is predominantly due to the poor charge transfer and separation ability, the short lifetime of the charge carriers (<10 ps), accompanying a short hole diffusion length (2–4 nm) [10], as well as slow water oxidation kinetics. Further improvements are highly demanded before the full potential of hematite can be reached for artificial photosynthesis devices.

To improve the solar water splitting efficiency of hematite materials a nanostructured morphology can be adopted, for example, nanorods or nanowire arrays [11], ultra-thin films [12], or thin films grown on three-dimensional (3D) nanotextured conducting substrates [13]. However, the nanostructured morphology strategy cannot speed up the slow water oxidation process, which limits the solar to fuel energy conversion efficiency. Surface modification of the photoanode with a co-catalyst, loading a surface passivation layer, or doing surface chemical corrosion were found to improve the overall system efficiency [14]. These methods may reduce charge recombination occurring at surface trapping states, promote separation and diffusion of carrier species and accelerate water oxidation kinetics [15]. Recently, forming heterojunctions at the nanoscale by coupling hematite to a second semiconductor has been evidenced as an effective way to engineer the band structure for enhanced optical absorption and promoting charge separation [15].

2. Surface Modification Strategies

In order to drive the water splitting reaction, the energy bands of the photoabsorber need to be properly aligned. Considering the invariable losses, the interfacial charge transfers and overpotentials for the molecular hydrogen and oxygen formation, a band gap of ~3.0 eV is required to make the reaction energetically favorable if using a single junction PEC device. Further, the band positions relative to the redox potentials of the electrolyte need to be considered. Figure 1a shows the energy levels of conduction band (CB) and valence band (VB) of hematite in respect to the reverse hydrogen electrode (RHE) and vacuum level (E_{vac}). It can be seen that hematite has a more positive CB edge than the hydrogen reduction potential, thus an external electrical bias is required to split water. This is the main reason for the required overpotential [1] as well as the positive V_{onset} . Bulk doping is an effective way to shift the V_{fb} and V_{onset} by changing the conduction and valence band levels [16]. However, details of bulk doping are beyond the scope of this review. Interested readers are referred to the review references [17,18]. Slow water oxidation kinetics are considered to be another reason for the positive V_{onset} . In order to enhance the water oxidation kinetics and reduce the applied potential, various surface modification strategies have been developed for hematite photoanodes. The effect of surface modification on a photoanode is schematically shown in Figure 1b. It can be seen that surface modification can reduce the V_{onset} for water oxidation, increase the photocurrent and, in some cases, reduce the V_{fb} . However, the effects and mechanisms of these surface modification strategies are quite different. For example, a non-catalytic surface passivation layer may reduce hematite surface charge trapping defects which reduces the electron-hole recombination rate, while a co-catalyst may mainly assist hole transport from the surface of hematite to the electrolyte [19]. In the next sections, various surface modification methods will be presented together with the resulting effects and proposed mechanisms.

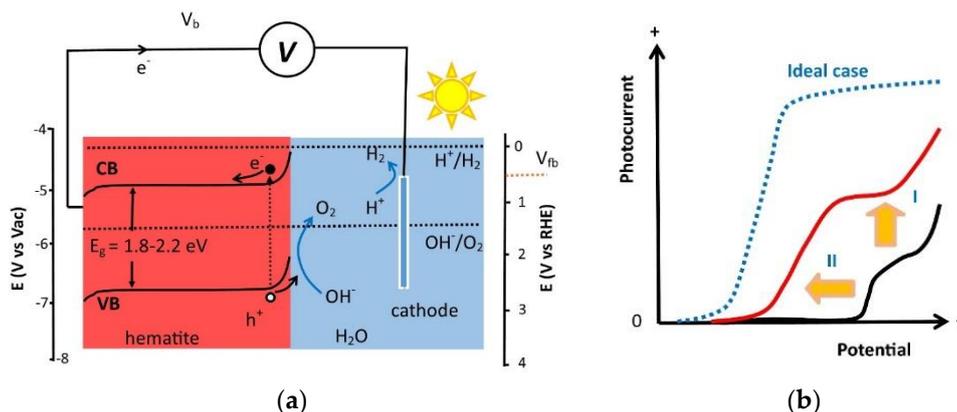


Figure 1. (a) Energy diagram for solar water splitting with a hematite photoanode performing the oxygen evolution reaction (OER) and a cathode carrying out the hydrogen evolution reaction (HER). The hematite bandgap (E_g), the flatband potential (V_{fb}), the applied bias (V_b), and the redox potential of water are indicated; (b) photoelectrochemical performance improvement of the hematite photoanode via surface modification. Arrow I indicates a photocurrent increase, arrow II indicates a photocurrent onset potential shift. The blue dotted line shows an idealized photocurrent vs. potential (I-V) of the hematite photoanode. The red line shows the I-V curve after surface modification while the back curve shows that of as prepared.

2.1. Co-Catalyst

In the past few years, the studies of co-catalyst loading including noble metal oxides and earth abundant metal oxides attracted great attention. Co-catalysts may promote separation and diffusion of charge carriers, thus decrease the recombination rate, reduce the overpotential required for the OER to occur, enhance the activity in the redox reactions, and in some cases provide a broadened absorption range. In this section, we will start with a review of noble metal based co-catalyst surface modification.

2.1.1. Noble Metal Based Co-Catalysts

As it is well known that the PEC efficiency is limited by the sluggish four-electron water oxidation kinetics [14,15], a great effort has been made to find a highly active and stable OER catalyst compatible with the harsh working conditions, e.g., a wide range of pH values or a high anodic potential. Noble metal oxides are the best available compromise between OER activity and stability at the moment. Several noble metal based co-catalysts have been developed to modify the hematite photoanode surface (see Table 1). These include IrO_2 [9], IrO_x [20,21], RuO_2 [22], RuO_x [23,24], Rh(OH)_x [25] and Pt [26]. For example, surface modification of nanostructured hematite photoanodes with 2 nm IrO_2 nanoparticles resulted in a 200 mV cathodic shift in the V_{onset} and an increase in the plateau photocurrent from 3.45 to 3.75 mA cm^{-2} [9]. Even with this success, they still found the V_{onset} of around 400 mV more positive than the V_{fb} , suggesting that surface states with mid-band-gap energies cause the carrier recombination in hematite. This further emphasizes that the continued optimization of both the nanostructure and the surface modification can ultimately achieve the full potential of solar water splitting using hematite. An electrodeposited IrO_x layer, which serves as a highly capacitive layer was reported to catalyze water oxidation by enhancing charge separation and storing photo-generated holes in hematite. This gave rise to a cathodic shift of 300 mV (see Figure 2) [20]. Similarly, Rh(OH)_x formed from the $\text{Na}_3\text{RhCl}_6 \cdot 12\text{H}_2\text{O}$ alkaline solution was also used to modify the hematite photoanodes, which resulted in a significant decrease of up to 200 mV in the overpotential due to efficient hole transfer from hematite to Rh(OH)_x [25]. Hematite modified with oxidized Pt species also shows a greatly enhanced photocurrent density for water splitting, mainly due to improved charge transfer and retarded carrier recombination [26]. Even though these noble metal or noble metal oxide decorated hematite photoanodes show a significant overpotential reduction and high stability, it has to be considered that noble metals are expensive and not abundant elements, making them unsuitable for

large-scale water splitting applications. Therefore, it is an essential step towards practical applications to find a cheap, efficient and scalable OER co-catalyst. In the next section, several earth abundant OER co-catalyst will be reviewed.

Table 1. List of noble metal co-catalysts used for surface modification on hematite nanostructures.
Note: ^a vs. NHE, ^b at 0.72 V vs. NHE (200 W Xe, 150 mW·cm⁻²), ^c 500 W xenon illumination.

Noble Metal	Preparation	Electrolyte	Onset Potential (V _{RHE})	Onset Potential shift (mV)	Photocurrent at 1.23 V _{RHE} (mA cm ⁻²)	Ref.
IrO ₂	Electrophoresis	1 M NaOH	0.8	200	~3.2	[9]
IrO _x	Electrodeposition	0.1 M KP _i (pH 7)	~1.1	300	0.2	[20]
IrO _x	Photoelectrodeposition	0.1 M KNO ₃ (pH = 1.01) 0.2 M NaOH	0.6	250	0.66	[21]
RuO ₂	Spray pyrolysis	containing 0.5 M Na ₂ SO ₄ (pH 13)	0.22 ^a	120	~0.68 ^b	[22]
Ru complex	Dip coating	1 M NaOH 0.1 M	0.72	~100	~2.2	[23]
Ru complex	Self-assembly	KHC ₈ H ₄ O ₄ -HCl buffer (pH 3)	0.7	~200	~0.12	[24]
Rh(OH) _x	Precipitation	1 M NaOH	~0.2	~300	1.5 ^c	[25]
Pt	Sputtering	0.1 M NaOH	0.8	No data	0.638	[26]

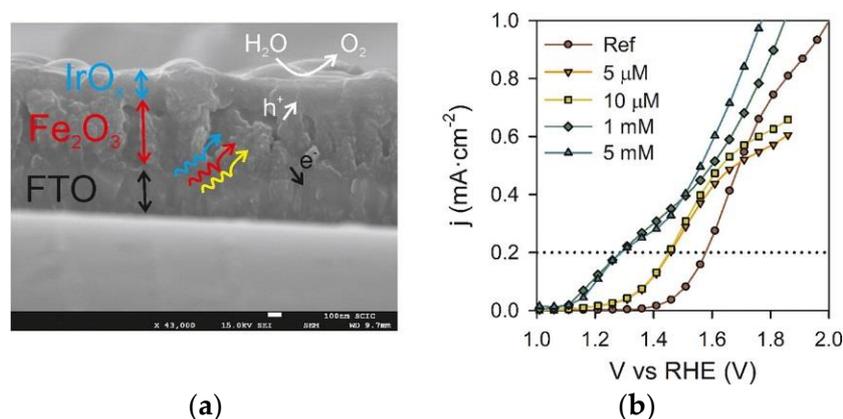


Figure 2. (a) Cross-section scanning electron microscope (SEM) image of fluorine doped tin oxide (FTO)/hematite and (b) steady-state I-V curves for bare hematite and after electrodeposition of pentamethylcyclopentadienyl (Cp^{*}) iridium(III) [Cp^{*}Ir(III)] from differently concentrated solutions (5 μM, 10 μM, 1 mM and 5 mM). The lines are used as eye guides. Reprinted with permission from Reference [20], copyright (2013) American Chemical Society.

2.1.2. Earth Abundant Metal Based Co-Catalysts

Several earth abundant transition metal oxides based e.g., on Co and Ni have been used to modify photoanodes serving as stable co-catalyst that increases the turnover frequency (TOF) (see Table 2). Amorphous cobalt oxide (CoO_x), named also Co-P_i, which is electrodeposited by the oxidation of Co²⁺ ions to higher oxidation state in a neutral phosphate buffer solution, shows many favorable properties for application as water oxidation catalyst [27]. This includes its facile synthesis procedure, low cost, neutral operation condition (pH 7), and a self-repairing mechanism. It has emerged as one of the most important OER co-catalysts and has been coupled with various photoanodes for effective PEC water splitting [28,29]. For example, an electrodeposited Co-P_i modified hematite photoanode shows a cathodic V_{onset} shift of 350 mV [30]. Scanning electron microscope (SEM) studies imply that the catalyst layer deposited conformally onto the mesostructured hematite results in a large contact area at the interface of the composite photoanode. The modification of the hematite film with a conformal layer of co-catalyst is proposed to allow the separation of the processes of photon absorption and redox catalysis.

This strategy has important and general ramifications for PEC hydrogen generation. The enhancement mechanism by Co-P_i incorporation was addressed in a systematic PEC and impedance spectroscopy study. The authors found that the Co-P_i co-catalyst can efficiently collect and store photo-generated holes from the hematite electrode, thus, reduces the surface state recombination [31]. They also found that thicker Co-P_i films lead to increased water oxidation efficiencies which they attributed to the superior charge separation as well as the increased surface area. Besides Co-P_i, there are also other Co-based co-catalyst modified hematite studies. Xi et al. found that in situ incorporation of the Co₃O₄ during hydrothermal growth of hematite nanorod arrays greatly improves the photocurrent and the incident photon-to-current efficiency (IPCE) of hematite photoanodes (see Figure 3) [32]. We recently investigated photoelectrodeposited CoB_i modified hematite nanorods combining PEC characterizations and in situ X-ray absorption spectroscopy (XAS) and found that the current density at 1.23 V of the bare hematite is 0.88 mA cm⁻² and increases to 1.12 mA cm⁻² after CoB_i co-catalyst modification (~27% improvement) [4]. Operando XAS studies showed that photo-generated holes gradually oxidize Co species into higher oxidation states, e.g., Co⁴⁺, in the CoB_i layer. The CoB_i co-catalyst layer is suggested to mainly improve OER kinetics and also to reduce electron-hole recombination at the surface, resulting in photocurrent enhancement and a cathodic shift of V_{onset}. Similar, nickel based co-catalysts have been applied to hematite photoanodes for efficient solar water splitting [33–37]. For example, photochemically deposited Ni-B_i on hematite nanorods resulted in a cathodic shift of >200 mV in the V_{onset} for water oxidation and a 9.5 times photocurrent enhancement at 0.86 V vs. RHE compared to the pristine material [34]. The authors found that the Ni-Bi modified hematite photoanode showed an encouraging improvement of photocurrent density near the V_{fb} of hematite. In another study, atomic layer deposited (ALD) Ni(OH)₂ led to a considerable reduction of the V_{onset} for water oxidation and a twofold improvement in photocurrent density at 1.23 V vs. RHE, which was effective for both the pristine and Ti-doped hematite photoanodes [36]. This enhanced performance is attributed to the improved charge separation with the ion-permeable Ni(OH)₂ catalyst film.

Table 2. List of earth abundant metal based co-catalysts used for surface modification on hematite photoanodes.

Transition Metal	Catalyst Preparation	Electrolyte	Onset Potential (V _{RHE})	Onset Potential shift (mV)	Photocurrent at 1.23 V _{RHE} (mA/cm ²)	Ref.	
Co	Co ₃ O ₄	in situ hydrothermal growth	1 M NaOH	0.66	40	1.20	[32]
	Co-B _i	photoelectrochemical deposition	0.1 M NaB _i (pH 9.2)	0.8	50	1.12	[4]
	Co-P _i	electrochemical deposition	1 M NaOH	~0.8	350	0.6	[30]
	Co-P _i	photoelectrochemical deposition	0.1M KP _i (pH 6.9) with 0.2 M KCl	~0.9	~240	0.4	[31]
Ni	Ni(OH) ₂	ALD	1 M KOH	0.9	~300	0.4	[36]
	Ni(OH) ₂	Dip coating	1 M KOH and 0.1 M glucose	0.7	~200	3.0	[33]
	NiOOH	Photoelectrodeposition	1 M NaOH	0.62	150	0.625	[37]
	Ni-B _i	Photodeposition	1 M NaOH	0.7	~200	0.55	[34]
	Ni-B _i	Photodeposition	1 M KB _i (pH~9.2)	0.6	140	0.65	[35]
Others	MnO _x	ALD	1 M NaOH	0.1.6	~100	<0.01	[38]
	FeNiOOH	Electrodeposition	1 M NaOH	0.57	190	2.21	[39]
	ZnCo LDHs	Electrodeposition	1 M KOH	~1.0	~100	1.73	[40]
	NiCo ₂ S ₄	hydrothermal method	1 M KOH	0.51	~330	1.51	[41]

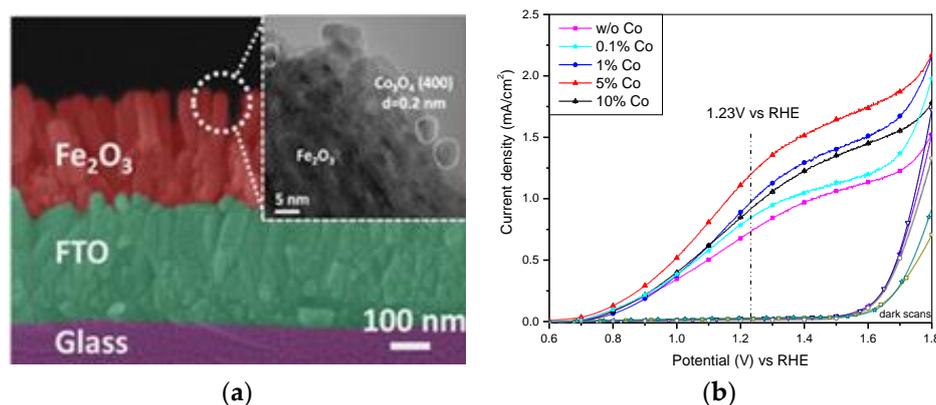


Figure 3. (a) Cross-section SEM image of hematite after annealing at 550 °C for 2 h and (b) I-V curves of hematite photoanodes with different amounts of Co^{2+} added to the precursor solution. Reprinted with permission from Reference [32], copyright (2012) American Chemical Society.

In the literature, other metal oxides, e.g., MnO_x [38], metal layered double (oxy)hydroxides [39,40] or sulfides [41] have been used as co-catalysts for hematite photoanodes to promote PEC performances for water splitting. For instance, electrodeposited FeNiOOH modified hematite resulted in a 190 mV cathodic shift in the V_{onset} as well as a great increase in photocurrent density from 0.9 to 2.24 mA cm^{-2} [39]. The electrochemical impedance spectroscopy (EIS) results show that the FeNiOOH co-catalyst decreases the charge transfer barrier and reduces the OER barrier, leading to a cathodic shift of the V_{onset} .

It can be seen that surface modification with co-catalysts is an effective strategy to facilitate the water photo-oxidation reaction by accommodating excited electrons/holes via the oxidation of the metal element of the co-catalyst, assisting photo-generated hole transport from the hematite to the electrolyte and facilitating redox reaction kinetics. This results in a cathodic shift of V_{onset} and an enhancement in the photocurrent for the solar water oxidation.

2.2. Enhancing Photoabsorption

The poor PEC performance of hematite is mainly due to a short lifetime of photo-generated minority carriers (holes, <10 ps) as well as a short diffusion length (2–4 nm) [10], resulting in significant non-radiative electron-hole recombination inside the hematite. The short diffusion length stands in conflict with the long absorption length of light (near the band edge in the micrometer regime) which greatly limits its PEC performance [14]. In recent years, several strategies including preparing ultrathin films, nanostructured hematite morphologies (nanorod, nanowire, nanopillar, nanotube and nanosheet), dual absorber heterostructures and 3D nanophotonic structured substrate/hematite photoanodes giving maximum possible photon absorption have been developed. Interested readers are referred to references [4–11,14,15,42]. Here, we will introduce two strategies, rare earth element and surface plasmonic metal decoration, to enhance photoabsorption of hematite photoanodes.

2.2.1. Rare Earth Element Decoration

Rare earth elements have attracted great attention in catalytic processes due to their optoelectronic properties arising from their unique electronic structure [43]. Infrared radiation accounts for a large share of the solar energy distribution. Current solar water splitting devices generally consisting of a semiconductor as photocatalyst, mainly absorb ultraviolet (UV) radiation and only to a much smaller extend visible light (see Figure 4) [44]. Adapting the optical properties of a solar water splitting device to the solar spectrum is a great challenge. One recent approach to improve the performance of photoelectrodes is to take advantage of the low energy photons in the infrared (IR) range [43,45]. Some of these rare earth elements, e.g., lanthanum, erbium or ytterbium, have the capability to absorb light in the infrared region and to convert them into shorter wavelength photons via a so-called up-conversion process, which effectively enhances the overall light harvesting and

photon management in the films [43]. For example, Zhang et al. attempted to exploit IR radiation, by casting a rare-earth element solution on top of hematite photoelectrodes [45]. Emission spectra evidence that the rare earth nanocrystals (REs) in the composite absorb at around 980 nm and emit photons at 550 and 670 nm. The emitted photons are absorbed by the surrounding hematite film, leading to a photocurrent enhancement from 25 to 130 nA cm⁻² and thus to an improvement of water splitting efficiency. In another study, it is proposed that drop-casted ytterbium oxide on hematite nanorod photoelectrodes induces the formation of a passivating layer that accounts for the great photocurrent enhancement [46]. However, it might be that here, the photoabsorption enhancement effect via up-conversion also plays a role.

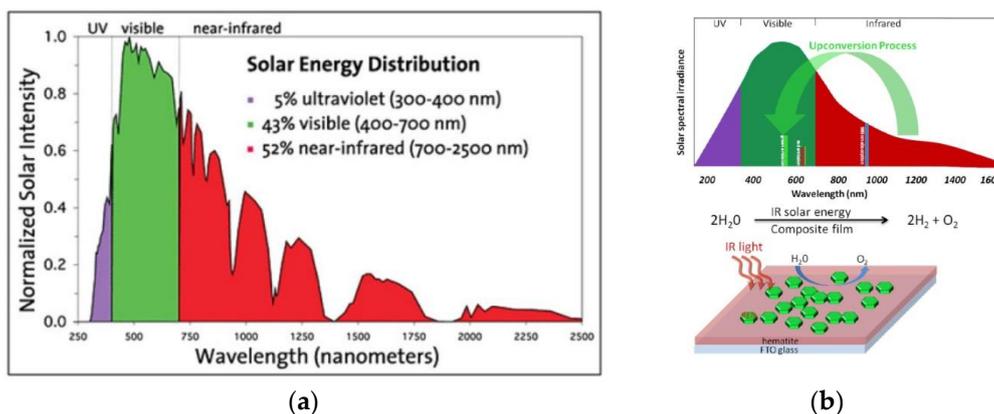


Figure 4. (a) Solar energy distribution and capture by a semiconductor photoabsorber; (b) mechanism of the up-conversion process (top) and enhanced solar water splitting performance by using near infrared radiation with the aid of rare earth materials (bottom). Reprinted from Reference [44].

2.2.2. Surface Plasmonic Metal Decorated Hematite

Surface plasmon polaritons (SPPs) are electromagnetic excitations coupled to the collective oscillations of free electrons on a metal surface, and thus can be considered to be surface electromagnetic waves propagating along the interface of a metal and a dielectric material [47]. The SPP electromagnetic field is confined to the vicinity of the metallodielectric boundary, resulting in a great field enhancement at the interface. For a plasmonic metal decorated semiconductor photoanode, the optical excitation of SPPs propagating at the nanostructured metallodielectric interface probably traps incident solar energy and transforms it into surface electromagnetic waves propagating along the photoelectrode surface, thus enhances the effective light path length as well as the absorption [47]. It probably also enhances solar absorption near the interface where the electromagnetic field is confined and amplified. Thus, SPPs are promising to overcome the dilemma of the requirement for hematite to be physically thin enough and optically thick enough for efficient solar energy-conversion.

In recent years, surface plasmonic nanostructures have been widely studied in enhancing the solar water splitting efficiency [48–50]. For example, the influence of gold nanoparticles on hematite photoanodes for solar water splitting was reported [49]. Only for electrode geometries with metal particles located at the semiconductor-electrolyte interface a relative enhancement was observed (see Figure 5) [49]. This is in agreement with the observation that minority carrier (holes) transport to the electrolyte is the most significant barrier to achieving high efficiencies in this system. In another study, three times higher light absorption and photocurrent improvement compared with the pristine hematite photoanodes are achieved from thin hematite films containing Au nanoparticles [50]. They found that the plasmonic enhancement goes along with an increase in the amount of Au nanoparticles for hematite films of constant thickness and is maximized for thin films. A thin hematite film can reduce the charge transport distance and have an optimal local field enhancement effect. The plasmonic resonance of metallic nanoparticles can also be adjusted through adjustment of the shapes or sizes to match the absorption bands of semiconductors [47]. It also strongly depends on the light incidence

angle. The disadvantage of surface plasmonic metal decoration is the usage of noble metal, thus the high cost and low abundance are critical issues.

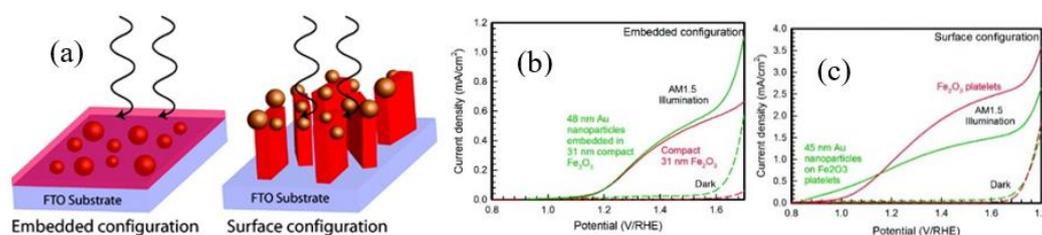


Figure 5. (a) Two different electrode configurations: Embedded and surface; (b) I–V curves for the embedded configuration and (c) I–V curves for the surface configuration. Reprinted with permission from reference [49], copyright (2011) American Chemical Society.

2.3. Surface Passivation

Even when using a nanostructured hematite combined with a surface incorporating oxygen evolution co-catalyst, a large overpotential is still required to drive water oxidation. This suggests that other factors besides slow OER kinetics or poor visible light absorption greatly affect the water splitting [42]. Surface states, also named interfacial states, are two-dimensional (2D) localized levels associated with the surface of hematite, which are caused by either oxygen vacancies or crystalline disorder [7,51]. Surface states are thought to be responsible for the recombination of photo-generated electron-holes before participating in the water oxidation reaction. However, they are also considered to transfer the photo-generated holes and accelerate the water oxidation reaction (see Figure 6) [51]. In order to improve charge separation at the hematite/electrolyte interface, introducing a surface passivation layer is an effective way to minimize the surface states. Representative surface passivation materials, such as Al_2O_3 [7,52,53], Ga_2O_3 [53], In_2O_3 [53], ZnO [54] and TiO_2 [55,56], have shown significant photocurrent improvements and resulted in a cathodic shift of V_{onset} (see Table 3). These studies showed that advantageous surface modifications of hematite can be achieved by safe, inexpensive materials as well as simple processing techniques. Established preparation methods are spin coating, ALD, hydrothermal and chemical bath deposition. For example, Le Formal et al. coated nanostructured hematite photoanodes with a very thin (0.1 to 2 nm) Al_2O_3 overlayer by ALD and found a significant decrease in the overpotential, due to the passivation of surface trapping states eliminating surface charge recombination [7,52]. Hisatomi et al. found that an Al_2O_3 , Ga_2O_3 , or In_2O_3 engineered overlayer created by facile chemical bath deposition can improve the V_{onset} of PEC water oxidation of hematite photoanodes [53]. These corundum-type overlayers were expected to release the lattice strain of the ultrathin hematite layer, reducing the surface state density. As revealed by transient absorption (TA) studies under applied bias, such cathodic shift of the V_{onset} , coincides with a similar cathodic shift of the occurrence of long-lived photo-generated holes, was due to slower electron-hole recombination, and primarily attributed to enhanced electron depletion in hematite [15]. Xi et al. previously reported that a very thin ZnO overlayer deposited by spin-coating on the surface of a hematite film was found to enhance the photocurrent by more than 40% and to induce a cathodic V_{onset} shift of 170 mV, compared to untreated hematite [54]. This improvement resulted from the altered V_{fb} and reduced surface defects. Yang et al. reported that an ultrathin ALD-grown TiO_2 overlayer on the hematite surface contributed to an obvious improvement in PEC water oxidation performance by cathodically shifting the V_{onset} up to 100 mV [55]. With electrocatalytic or bulk doping effects ruled out, this PEC improvement was attributed to better charge separation, fewer surface charge recombination, and thus greater photovoltage induced by the TiO_2 overlayer. A greater cathodic shift of 250 mV in turn-on potential was achieved over hematite photoanodes with surface passivated by a TiO_2 overlayer via an ALD method [56]. TA spectroscopy shows that the enhanced PEC responses of heterostructured photoanodes are mainly due to an enhanced charge separation.

Table 3. List of materials and preparation methods used for surface passivation on hematite nanostructures.

Passivation Materials	Preparation	Electrolyte	Onset Potential (V_{RHE})	Onset Potential shift (mV)	Photocurrent at $1.23 V_{\text{RHE}}$ (mA cm^{-2})	Ref.
Al_2O_3	CBD	1 M NaOH	0.91	200	0.4	[52]
Al_2O_3	ALD	1 M NaOH	0.8	100	2.8	[7]
Al_2O_3	ALD	1 M NaOH	0.97	~90	~2.2	[53]
Ga_2O_3	CBD	1 M NaOH	0.8	~210	~0.45	[52]
In_2O_3	CBD	1 M NaOH	0.89	~100	~0.47	[52]
ZnAc	Spin coating	1 M NaOH	0.76	170	1.08	[54]
TiO_2	ALD	1 M NaOH	~0.9	100	1.014	[55]
TiO_2	ALD	1 M NaOH	0.8	~250	2	[56]
NaPO_2H_2	Decompose	1 M NaOH	0.7	100	1.1	[57]
CTAB	Hydrothermal	1 M KOH	0.6	0	0.45	[58]

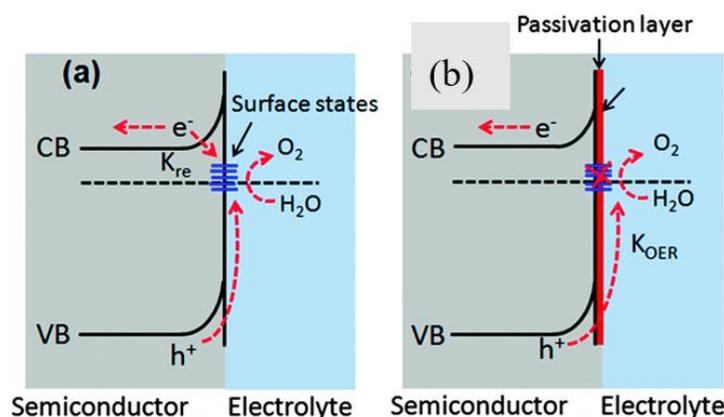


Figure 6. The band structures of an n-type semiconductor photoanode (a) without and (b) with a passivation layer. (a) High charge recombination happening at surface defects and thus inefficient water oxidation by the photo-generated holes; (b) use of thin non-catalytic passivation layers which suppress surface recombination and improve water oxidation. Adapted from Reference [14], copyright (2016) Royal Society of Chemistry.

Additionally, non-metal surface passivation of hematite using e.g., phosphorus [57], or bromide [58] were previously presented. It was shown that amorphous phosphorus is able to passivate surface states of a hematite nanorod photoanode and to suppress electron-hole recombination, significantly enhancing the photocurrent for water oxidation [57]. It is proposed that cetyltrimethylammonium bromide (CTAB) modification of the hematite surface leads to an increase of carrier density favoring the transport of the charge carriers [58]. The Br-layer induced negative electric field created on the hematite surface is assumed to speed up the interfacial charge transfer and the OER kinetics leading to an enhancement in the solar water splitting performance.

2.4. Surface Chemical Etching

Surface chemical etching, e.g., etching with HF [59], HCl [60,61] or H_2 [62], can remove native and/or amorphous oxides and change the chemical state of the surface of the electrode, thus potentially improve the surface conductivity and photocurrent. Hematite is generally accepted to be kinetically stable under oxidizing conditions, hence surface etching may help to passivate surface states and facilitate the water oxidation at low applied potentials [14,19]. An HF treatment on hematite nanowires etches away the amorphous iron oxide phase at the surface, leading to a single crystalline surface and a reduction of the V_{onset} by 300 mV [59]. Rioult et al. found that the HCl etching does not contribute any amorphous structure removal [60]. They found that partial HCl wet-etching has a great effect on the morphology of the hematite films, but also on the electronic structure and the oxidation state. Recently, H_2 -treated hematite nanostructures were deposited by a simple pyrolysis

of sodium borohydride (NaBH_4) in a crucible [62]. The H_2 -treated photoanode showed more than 2.5 times photocurrent density enhancement and 120 mV cathodic shift in the V_{onset} than that of the pristine hematite. The authors attributed the photocurrent increase to an increased number of oxygen vacancies, while they correlated the cathodic shift of the V_{onset} to the surface effect of H_2 treatment. Using CoF_3 aqueous solution as an etching agent for Ti-doped hematite photoelectrode was also reported [63]. The authors proposed that the adsorption of fluoride on the surface of the electrode shifts the CB to a more negative potential than the redox level of H_2/H^+ . This allows the photo-generated electrons to directly reduce water to H_2 . There are also other etching agents to remove surface defects [64,65]. Table 4 summarizes recent surface etching works for hematite photoanodes.

Table 4. List of surface chemical etching for surface modification on hematite nanostructures. Note: ^a directly oxidizing Fe foil in a $\text{H}_2\text{-O}_2$ flame at around 1700 K.

Modification Material	Preparation	Electrolyte	Onset Potential (V_{RHE})	Onset Potential Shift (mV)	Photocurrent at 1.23 V_{RHE} (mA cm^{-2})	Ref.
HF	Dip in HF solution	1 M KOH	~0.8	No data	~0.18	[59]
HCl	Dip in HCl solution	0.1 M NaOH	~1.0	100	~1.0	[60]
HCl	Dip in HCl solution	1 M NaOH	0.87	100	1.5	[61]
NaBH_4	Pyrolysis by NaBH_4 solution	1 M NaOH	0.87	120	2.28	[62]
CoF_3	Dip in CoF_3 solution	1 M NaOH	0.6	200	~1.5	[63]
$\text{H}_2\text{-O}_2$ ^a	React in a $\text{H}_2\text{-O}_2$ flame	1 M NaOH	0.50	No data	~0.45	[64]
Oxalic acid	Dip in oxalic acid solution	1 M NaOH with and without H_2O_2 added	~0.7	<20	~1.4	[65]

2.5. Surface Doping

Surface doping with metal ions is an alternative way to obtain an enhanced PEC performance of hematite photoanodes [14]. It possibly promotes charge migration, broadens the absorption range and/or creates a doped overlayer to catalyze the surface water oxidation reaction. Several studies demonstrated that surface-engineered hematite nanostructures with metal ion doping, e.g., Sn^{4+} [11], $\text{Ni}^{3+/4+}$ [66] or Ag^+ [7], exhibited a considerable photocurrent density enhancement and cathodic V_{onset} shifts [15] (see Table 5). Xi et al. treated hydrothermally grown iron oxyhydroxide nanorod arrays with Sn^{4+} aqueous solution before subsequently annealing it at high temperature [11]. The formation of a $\text{Fe}_x\text{Sn}_{1-x}\text{O}_4$ thin layer on hematite nanorod arrays by surface Sn doping is assumed to passivate surface defects, thus to reduce electron-hole recombination at the interface of hematite–electrolyte, as well as to suppress the electron tunneling from the hematite core. Later, similar to this approach, a hematite nanotube photoanode doped with a thin $\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$ overlayer on the surface showed a 280% enhancement of the photoconversion efficiency compared to the pristine hematite nanotube film (see Figure 7) [66]. The authors proposed that the $\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$ overlayer was attributed to the facilitated charge migration, accelerated oxygen evolution, and avoiding the photoexcited hole recombination at the interface of hematite and electrolyte [14,66]. Recently, an $\text{Ag}_x\text{Fe}_{2-x}\text{O}_3$ passivation layer with a thickness of 2–3 nm along hematite nanorods was reported for surface doping of Ag ions [67]. The authors claimed that the Ag-doped passivation layer increases the charge carrier density in the near-surface region and accelerates the kinetics of the surface oxidation reaction, synergistically contributing to the improved PEC performances.

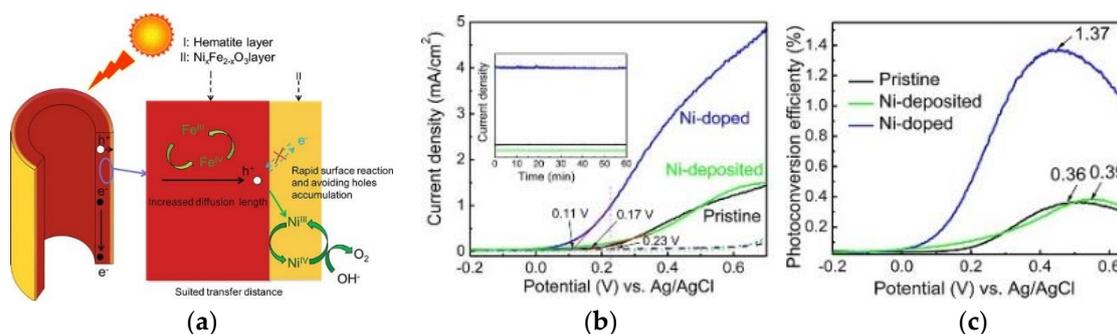


Figure 7. (a) Schematic of the OER process taking place at the hematite photoanode. In the sketch map, it only shows the OER process occurring on the outside surface of the hematite nanotube wall covered with the $\text{Ni}_x\text{Fe}_{2-x}\text{O}_3$ thin layer. The authors admitted that the same process also occurs on the inside surface; (b) current density (inset: Photochemical stability curves); and (c) incident photon-to-current conversion efficiency (IPCE) curves of the pristine, Ni-deposited and Ni-doped samples. Reprinted with permission from Reference [66], copyright (2012) American Chemical Society.

Table 5. List of surface doping for surface modification on hematite nanostructures.

Modification Material	Preparation	Electrolyte	Onset Potential (V_{RHE})	Onset Potential Shift (mV)	Photocurrent at 1.23 V_{RHE} (mA cm^{-2})	Ref.
Sn^{4+} aqueous solution	Drop the solution on top and then anneal at high temperature	1 M NaOH	0.62	100	2.25	[11]
Ni^{2+} aqueous solution	Electrodeposit and then anneal at high temperature	1 M KOH	~1.0	100	~1.0	[66]
Ag^+ aqueous solution	Dip in the Ag^+ solution, dry and then anneal at high temperature	0.5 M NaCl (pH 6.7)	0.40	100	~0.1	[67]

3. Conclusions and Outlook

Due to its moderate band gap, chemical stability, non-toxicity, abundance, and low cost, hematite is a promising photoelectrode material for solar water splitting. However, it suffers from poor charge transfer and separation ability, short hole diffusion length as well as slow water oxidation kinetics. Several surface modification methods have been developed to improve slow water oxidation kinetics and the range of light absorption in the past decade. In this review, several of these surface modification techniques were reviewed. They include loading of co-catalysts, decorating with rare earth metal oxides or surface plasmonic metal oxides to enhance photoabsorption, applying a surface passivation layer, surface chemical etching and surface doping. Although significant progress in surface modification has been made, continuous innovations and new studies of surface modification using operando methods, e.g., UV-Vis, XAS, XPS and SEM are essential to meet the request for the development of efficient photoanodes using hematite and to drive the solar water splitting into practical application. In particular, future studies are highly demanded to explore new surface modification materials and methods [42,68]. A limited material and method selection may not meet the demands for obtaining highly efficiency solar water oxidation devices. We prospect that in the near future, a combination of different modification strategies, as well as nanostructure and semiconductor engineering, may greatly help to generate strong synergistic effects for further PEC performance improvement [15].

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