

Typical strategies to facilitate charge transfer for enhanced oxygen evolution reaction: Case studies on hematite

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Abstract: Hydrogen can be sustainably produced through photoelectrochemical (PEC) water splitting. The process of PEC water splitting is composed of two vital half-reactions: water oxidation to O₂ on photoanode, and proton reduction to H₂ on photocathode. Both in thermodynamics and kinetics, the oxidation of water on photoanode is much more challenging, because the formation of O₂ involves the four-holes reaction process that is more difficult than the two-protons reduction. Accordingly, the oxidation of water into O₂ is the rate-determining reaction for PEC water splitting, which is closely affected by the light harvesting, charge separation and transfer, as well as surface activity of photoanode. In principle, water oxidation is initiated by the photo-excited charge of photoanode. In this review, we took hematite photoanode as a typical example to illustrate the progress in modifying the charge separation and migration property of metal-oxide photoanodes for water oxidation. The typical strategies adopted to facilitate the charge transfer and separation of hematite photoanode were specifically summarized. In addition, the views designing and developing hematite photoanode with high-performance for water oxidation were presented. This review provides comprehensive information about the state-of-the-art progress of hematite-based photoanodes and forecast the developing directions of photoanode materials for solar water splitting.

Key words: water splitting; hematite photoanode; charge transfer; modification strategy

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1. Introduction

The realization of a zero-carbon society to address the energy and environmental issues has remained a great technical challenge. The utilization of solar energy, an inexhaustible natural energy source, is the ultimate option remaining to tackle the increasing global energy demands of modern society^[1, 2]. Photoelectrochemical (PEC) water splitting is a green technology to achieve the production of H₂ energy from solar energy, which has aroused extensive research interests since the report of H₂ and O₂ generation in TiO₂ photoelectrode-based cell in 1972^[3, 4]. The principle of PEC water splitting in an n-type photoelectrode-based cell is shown in Fig. 1, which primarily involves three main steps: (1) Under solar illumination, when the n-type semiconductor electrode absorbs the photons with energy higher than its band gap, the electrons and holes are produced in its conduction and valance band, respectively. (2) If the valence band position of the n-type photoelectrode located above the potential of water oxidation (1.23 V vs. RHE), its photogenerated holes would transfer to the surface of photoelectrode, and subsequently react with water molecules for the formation of oxy-

gen. (3) In the meantime, the electrons of photoelectrode would be transferred to the counter electrode. Once the conduction band position of photoelectrode or the potential applied on the counter electrode is lower than the proton-reduction potential (0 V vs. RHE), the hydrogen evolution reaction would be initiated on the counter electrode. In a word, the oxidation and reduction half reaction occur separately on the anode and cathode of PEC water splitting cell, which is advantageous for the collection of O₂ and H₂ during water splitting. Relative to proton reduction, water oxidation is a kinetic difficulty process, as the formation of one O₂ molecule involves four holes oxidation. Accordingly, water oxidation on photoanode has been demonstrated to be the rate-determining reac-

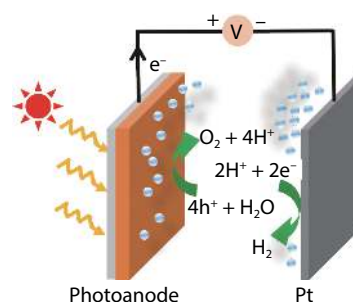


Fig. 1. (Color online) Schematic of water splitting in photoanode-based PEC cell.

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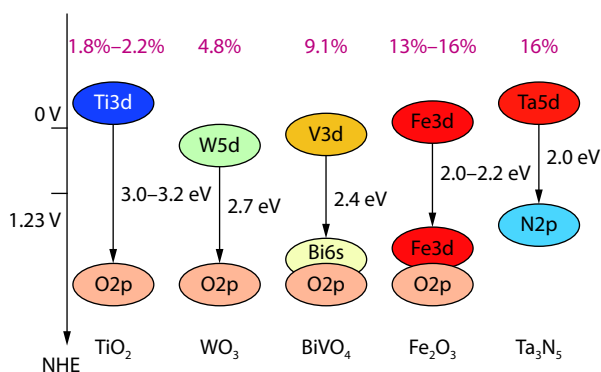


Fig. 2. (Color online) Ultimate photocurrent density and corresponding maximum STH of some semiconductors.

tion for PEC water splitting^[5–8]. In essence, the breakthrough direction of solar water oxidation is exploring suitable photoanode materials. In theory, the photoanode material being of the following properties would be the satisfactory candidate for water oxidation, (1) wide range of solar light absorbing, (2) good stability in aqueous solution, (3) efficient charge separation and transfer, (4) suitable conduction and valence band edges, (5) high surface activity for water activation, (6) low preparation-cost^[9]. Among the candidates of photoanode material, several metal-oxide semiconductors (e.g. anatase TiO_2 , monoclinic WO_3 , monoclinic BiVO_4 , hematite Fe_2O_3) meet partial above requirements and show potential application prospects.

Among the metal oxide photoanode materials (Fig. 2), hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a typical metal oxide photoanode, owing to its intrinsic advantages of nontoxicity, favorable valence band position, good stability in aqueous solution, and narrow bandgap. Hematite has a band gap of about 2.1 eV, and thus a theoretical solar-to-hydrogen (STH) efficiency high as 15.4% can be achieved on hematite photoanode, which is higher than the commercial requirement STH efficiency (10%)^[10–12]. Unfortunately, the practical STH of hematite photoanode is still far from its theoretical efficiency owing to the poor charge separation and transfer behaviors. At present, the modifications on charge transfer and separation properties are the main research direction for hematite photoanode. To date, several modified approaches have been developed to enhance the solar water oxidation activity of hematite photoanode with varying degrees of success. In recent years, several reviews have summarized the momentous progresses in hematite photoanode modifications. Gratzel's research group summarized the basic properties as well as the challenges of hematite photoanode for solar water splitting in their review published in 2011^[13]. Wheeler *et al.* reviewed the synthesis progress of nanostructured hematite for PEC water oxidation in 2012^[14]. With the rapid development of hematite photoanode research, new progresses in the modifications of charge transfer and separation properties are emerging. It is necessary to summarize these new progresses in hematite photoanode for understanding the trend of development. In the present review, we summarize the typical strategies that have been exploited towards high-efficiency water oxidation on hematite photoelectrodes, and hope to inspire new ideas for developing high-performance hematite photoanode. The photoelectric properties of hematite are briefly presented, and the challenges in exploiting high-per-

formance hematite photoanode for solar water splitting is outlined. The typical modified strategies that are employed to facilitate the charge transfer and separation of hematite photoanode for water oxidation, as well as investigations and understanding of oxygen evolution mechanism on hematite were significantly highlighted.

2. Advantages and limitations of hematite photoanode for solar water splitting

It is generally accepted that the water oxidation efficiency of photoanodes is affected by three synergetic processes: light absorbing; the separation of photogenerated electron-hole pairs (charge separation efficiency), photogenerated holes reacting with water molecules at photoanode/electrolyte interface (charge injection efficiency). For the hematite photoanode with a band gap of ~ 2.1 eV, its theoretical water oxidation photocurrent under standard solar illumination is 12.5 mA/cm^2 ^[13, 15, 16]. However, the practical photocurrent of hematite photoanode for water oxidation is still by far lower due to its insufficient charge separation and transfer^[17, 18]. Specifically, the light penetration thickness of hematite at 550 nm is about 118 nm, while its hole diffusion length is only 2–4 nm^[19–23]. Therefore, it is hard to achieve expectant charge generation and separation in a hematite with flat geometry, since thicker hematite film has higher recombination of carrier, while thinner hematite film has weaker light absorption. In theory, only the holes generated in the few nanometers thickness of the photoanode/electrolyte interface could survive for water oxidation, the others have to recombine with electrons. Hence, the charge separation efficiency of hematite photoanode is mainly limited by its short length of holes-diffusion^[24–26]. In addition, since the $\text{Fe}^{3+}/\text{Fe}^{2+}$ valence alternation on spatially localized 3d orbitals, the conductivity of hematite is only in the order of $10^{-2} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ (at 25 °C). The poor conductivity of hematite also has negative influence on its charge separation and transfer efficiency significantly. The third factor that limits the water oxidation activity of hematite photoanode is its sluggish kinetics in OER. As the $\text{Fe}^{3+} e_g$ level in hematite lies above the top of O 2p⁶ band, instead of the O 2p⁶ band itself, the photogenerated holes could be captured rapidly by $\text{Fe}^{3+} e_g$ level and results in the sluggish OER kinetics on hematite photoanode^[27]. Before the holes reaching the electrolyte interface and reacting with water molecules, the surface trap states of hematite photoanode could trap the holes preferentially^[28]. To overcome above drawbacks, various strategies have been focused on facilitating charge transfer and separation to achieve targeted water oxidation performance on hematite photoanode in recent years. The typically effective strategies include nanostructuring, doping, building junctions, and surface engineering, all of them aim to shorten the carrier migration path, boost the lifetime of photogenerated holes, and augment the OER kinetics of hematite photoanode.

3. Typical strategies towards improving the charge transfer of hematite photoanode

To erase or attenuate above-mentioned issues that restrict the charge separation and transfer efficiency of hematite photoanode, several effective strategies are developed. For example (a) Nanostructuring of hematite increases the ef-

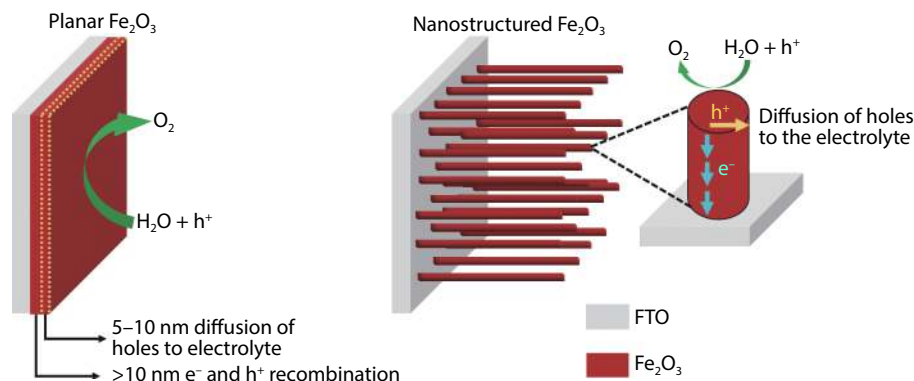


Fig. 3. (Color online) Comparison of electron–hole recombination in planar and 1D Fe_2O_3 nanorods arrays electrode.

fective surface area and reduces the holes' lifetime. (b) Doping of hematite improves its conductivity, extends its holes' lifetime, as well as reduces the electron–hole pairs recombination. (c) Loading of cocatalysts on hematite boosts its OER kinetics and improves the charge separation and transfer for water oxidation. (d) Surface passivating of hematite weakens the surface charge recombination. (e) Building heterojunctions enhance the charge separation and transfer efficiency of hematite through the heterojunction potential difference. The typical works and findings that related to above modified strategies for hematite photoanode are summarized as follows.

3.1. Nanostructuring

The short length of holes-diffusion (2–4 nm) in hematite critically suppresses the development of thick hematite film for effective light harvesting. As depicted in Fig. 3, although planar Fe_2O_3 film can realize a long light penetration depth, it simultaneously causes severe recombination of photogenerated holes during water oxidation, when the diffusion length of holes exceeds 10 nm film thick. As such, the photocurrent of planar hematite electrodes is not still improved by increasing the film thickness. To overcome the contradiction, hematite photoanodes with porous structures or 1D nanostructures have been prepared by morphology controlling methods. These nanostructured hematite film compared with planar hematite films have following potential advantages (as nanostructured Fe_2O_3 shown in Fig. 3): (1) Controlled film thickness for completing light absorption; (2) The smaller diameter of porous structures or 1D nanostructure for facilitating holes to reach electrolyte interface; (3) Larger specific surface area for the water molecules adsorption, dehydrogenation and activation^[29, 30]. To date, significant progress in increased PEC activity of hematite photoanode has observed on different hematite nanostructures owing to their improved charge separation and transfer efficiency. For instance, Yang *et al.* prepared $\alpha\text{-Fe}_2\text{O}_3$ nanobelts arrays with 30 to 300 nm in width and 5 to 50 μm in length, which significantly improves the charge separation ability of hematite^[31]. Recently, Lee *et al.* prepared single-crystalline wormlike hematite nanorod arrays on FTO by first forming 1D $\beta\text{-FeOOH}$ nanorods as the precursor and then converting them to $\alpha\text{-Fe}_2\text{O}_3$ by two-step annealing treatment. Since the 1D nanorod structure minimized the diffuse of holes to the photoanode/electrolyte interface and presented high crystallinity, the hematite photoanode showed a record-breaking performance of

4.32 mA/cm^2 photoelectrochemical water oxidation current at 1.23 V vs. RHE under simulated 1 sun irradiation^[21]. Most recently, Gong *et al.* successfully synthesized Zr- Fe_2O_3 nanotube arrays that survive high-temperature calcination for the first time by a solid-state reaction between hydrothermal FeOOH nanorod core and atomic layer deposition (ALD) ZrO_2 shell of suitable thickness. As a result of the nanostructuring and shortened charge collection distance, the nanotube photoanode showed a greatly improved PEC water oxidation activity^[32]. The same year, Yat *et al.* prepared hematite nanowire arrays without any shrink after a high-temperature annealing by a silica encapsulation method. The capability of retaining nanowires morphology allowed tuning the nanowire length for optimal light absorption and diameter for boosting the charge transfer and separation^[33]. Moreover, other especial 1D nanostructure arrays of hematite had developed. For example, Jia's group synthesized tube-in-tube hematite nanostructures through a facile hydrothermal method. Their investigations showed that hematite with tube-in-tube nanostructures had low charge recombination rate, because these interesting nanostructures can shorten the charge diffusion distance to the hematite/electrolyte interface^[34]. Cvelbar *et al.* reported perpendicularly aligned $\alpha\text{-Fe}_2\text{O}_3$ nanowires and nanobelts^[35], and so on. Recently, our group fabricated robust Fe_2O_3 porous nanopillar arrays through quasi-topotactic transformation of FeOOH nanorod arrays (as shown in Figs. 4(a)–4(d)). The obtained single crystalline porous nanopillar arrays not only decrease charge-carrier recombination, but also shorten holes transport distance from the bulk material to electrode-electrolyte interface. Thus, the porous Fe_2O_3 nanopillar arrays photoanode exhibited a photocurrent density as high as 2.0 mA/cm^2 at 1.23 V vs. RHE without using any cocatalysts (Fig. 4(e))^[36].

In terms of charge separation and transfer efficiencies, as everyone knows that 1D nanostructures exhibit superior performances in PEC devices compared to other nanoarchitecture arrangements (e.g., 2D-nanostructures or 3D-nanostructures), but in special cases, these nanostructures are also beneficial to charge transport. For example when 2D-nanostructures (such as nanoflakes, nanoplatelets, etc.) perpendicularly oriented to the electrode, this arrangement can enhance charge transport through the directional transport of charge to the substrate, and reduce the charge recombination using the ultrathin thickness of 2D nanomaterials^[37–40]. For 3D-nanostructures, the special representative case is a hierarchical nanostructure, in general, which consisted of an obvi-

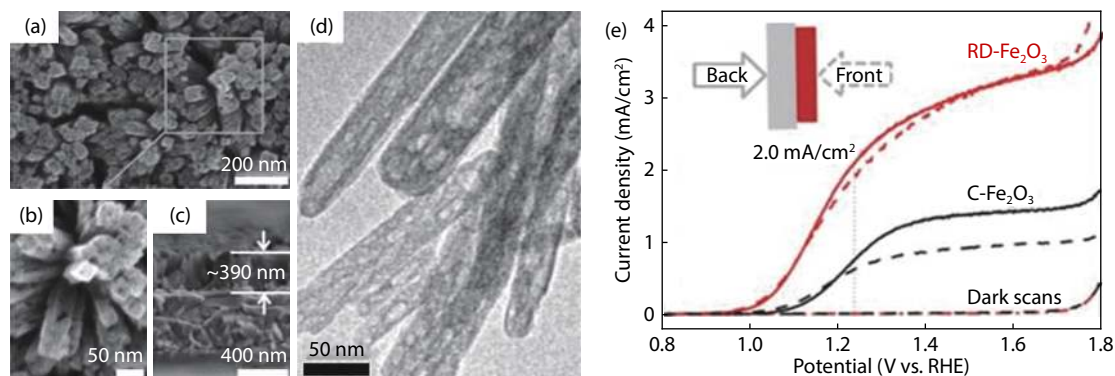


Fig. 4. (Color online) (a–c) SEM and (d) TEM images of obtained Fe₂O₃ by a facile rapid dehydration strategy (RD-Fe₂O₃). (e) Current density–voltage curves of obtained Fe₂O₃ by a conventional temperature-rising route (C-Fe₂O₃) and RD-Fe₂O₃ collected at 10 mV/s in 1.0 M KOH aqueous electrolyte under AM 1.5G illumination and in the dark. The solid and dashed lines represent the data collected under back (solid lines) and front (dashed lines) illuminations, respectively. Reproduced from Ref. [36].

ous backbone (typically with a 1D-arrangement) onto which nanodimensional building blocks are grown—these usually include nanoparticles, nanowires/rods/tubes and nanosheets hierarchical nanostructures^[41–43]. For example, TiO₂ nanorod arrays branched on 1D α -Fe₂O₃ nanorod arrays, which combine the advantages of α -Fe₂O₃ (such as, directional separation and transport of charge) and TiO₂ (such as, increased active sites). Therefore, TiO₂-on- α -Fe₂O₃ hierarchical nanotrees electrode achieved an enhanced photocurrent compared to the α -Fe₂O₃ and TiO₂^[44]. Moreover, 3D branched Fe₂O₃ nanorod arrays was prepared by a two-step conventional hydrothermal synthesis. The dendritic nanostructure of this photoanode with an increased solid–liquid junction area further improved the surface charge collection efficiency, generating a photocurrent of about 2.5 mA/cm² at 1.23 V vs. RHE under air mass 1.5G illumination^[45].

The section review shows the progress in morphology from thicker planar films to various 1D nanostructures, and then to recently special 2D or 3D nanostructure to improve the tradeoff between poor carrier collection and poor light absorption of hematite. It indicates nanostructure strategy is unquestionably well substantiated to promote the charge separation and transfer efficiency and thus enhancing PEC performance of hematite photoanode. So, continuing to design and fabricate peculiar and new nanostructures for high charge separation efficiency of photoelectrode is one of the key research goals.

3.2. Doping

When considering hematite for solar PEC water splitting, suitable elements doping is considered as an effective strategy to alleviate its bulk carrier recombination, since doping can improve the charge carrier mobility and concentration. In the recent reports, a beneficial effect of various dopants (such as Ti⁴⁺^[46, 47], Zr⁴⁺^[48], Si⁴⁺^[49], Sn⁴⁺^[50], Nb⁵⁺^[51], and W⁶⁺^[52], etc.) on the charge separation and transfer of hematite have been demonstrated. Among the n-type metal dopants for hematite, for example, Pu *et al.* observed a higher photocurrent of 2.25 mA/m² at 1.23 V vs. RHE upon Ti doped hematite for water oxidation. Although no surface structure and morphology changes observed on the Ti doped hematite, the donor concentration of hematite was significantly increased after Ti⁴⁺ doping, which results in the improved PEC

water oxidation activity^[46]. Our group also observed that the donor concentration of Fe₂O₃ film is increased 20 times after Ti-doping compared with the undoped Fe₂O₃^[47]. Furthermore, Horowitz *et al.* reported Zr⁴⁺ doped into α -Fe₂O₃ single crystals resulted in one order of magnitude higher donor densities, which implied after doping high the conductivity of α -Fe₂O₃^[48]. Among the non-transition metal dopants for hematite, Sn and Si have been demonstrated to be effective dopants^[49, 50]. Lukowski's group reported that Si-doped hematite nanowire arrays have a donor density of $4 \times 10^{-3} \pm 6 \times 10^{-3} \Omega \text{ m}$, while the donor density of the undoped samples is $4 \times 10^2 \pm 4 \times 10^2 \Omega \text{ m}$ ^[49]. As a result, the increased donor density in Si-doped hematite results in its higher photocurrent. To reveal the effect of conductivity of hematite on its charge transport and charge injection, Ling *et al.* prepared Sn-doped α -Fe₂O₃ through thermally-induced diffusion of Sn from the substrate, and measured the donor density of Sn-doped α -Fe₂O₃ is $5.38 \times 10^{19} \text{ cm}^{-3}$, $1.89 \times 10^{19} \text{ cm}^{-3}$ for the undoped α -Fe₂O₃^[50]. Soon afterwards Tamirat *et al.* found that the diffusion of Sn lead to the formation of a typical gradient doping which created steeper voltage gradients and helps to improve the carrier separation. Thus, these two factors, including improved electrical conductivity and created steeper voltage gradients, enhanced photoelectrochemical performance of hematite^[18]. However, the PEC performance of mono-doping is usually constrained by a limited doping concentration, which results from the radius mismatch between the doped ions and Fe³⁺^[53]. Moreover, some researchers argued that part-occupied mono-doping levels act as recombination centers of carriers, leading to decreased charge mobility and reduced excited carriers^[54].

Due to the disadvantages of mono-doping, two- and multi-ion doping have caught extensive attention. Recent studies have been demonstrated that hematite co-doped with two cations has higher activity than that doped with single cation because two ions doping could significantly reduce the recombination centers and effectively improve the charge migration efficiency^[55]. In the work of Tamirat' group, gradient Sn doped hematite achieved a photocurrent of 0.86 mA/m² at 1.23 V vs. RHE. When it co-doped with Zr, the photocurrent of hematite was further improved to 1.34 mA/m² (as shown in Fig. 5(b)). This improvement could be attributed to the synergetic effect of Sn, Zr co-doping that significantly mod-

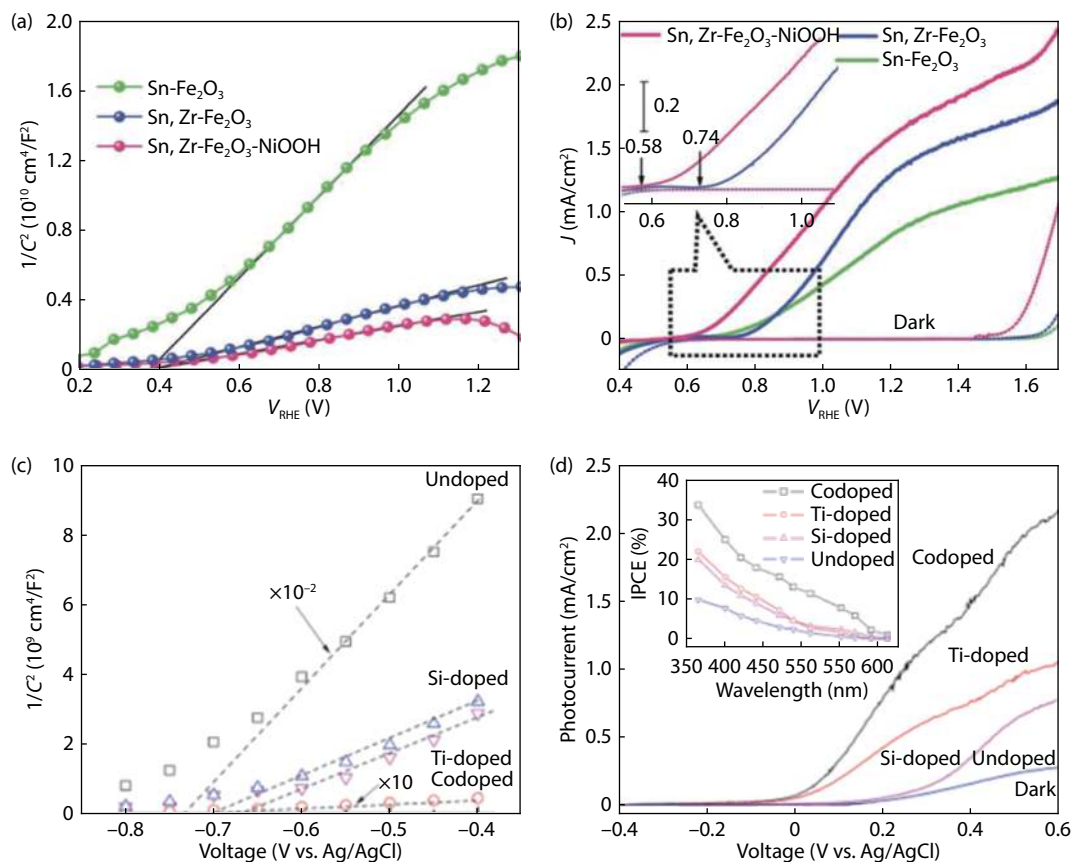


Fig. 5. (Color online) (a) Mott-Schottky (M-S) plots measured in 1 M NaOH solution. Conditions: 1 kHz frequency. (b) J - V curves of Sn-doped (green), Sn, Zr-doped α - Fe_2O_3 (blue), and Sn, Zr-doped α - Fe_2O_3 -NiOOH (red) in the dark and under illumination. Reproduced from ref 18. (c) M-S plots of undoped, Si-doped, Ti-doped, and co-doped α - Fe_2O_3 films at the frequency of 1000 Hz. (d) J - V characteristics of the undoped, Si-doped, Ti-doped, and co-doped films in 1 M NaOH under 500 W full arc xenon lamp, the green line indicates dark currents of all the films. The inset is IPCE performance for the four α - Fe_2O_3 films mentioned above at 0.6 V vs. Ag/AgCl in 1 M NaOH. Reproduced from Ref. [56].

ified the conductivity of hematite and increased its charge carrier density more than three times (Fig. 5(a)) relative to the Sn doping^[18]. Our group also reported Si and Ti co-doped hematite photoanodes with higher PEC activity for water oxidation. Since Si and Ti co-doping can not only balance the ion radius difference between Fe^{3+} and Si^{4+} or (Ti^{4+}) but also increase the donor concentration (as evidenced from Mott-Schottky analysis (Fig. 5(c))^[56]. Therefore, the IPCE of Si, Ti co-doped hematite film achieved to 34% at 365 nm and 0.6 V vs. Ag/AgCl, which is higher than 10%, 20%, and 22% for the undoped, Si-doped, and Ti-doped hematite, respectively (Fig. 5(d)). Recently, Xie's group reported the photocurrent density of Sn-/Mg-co-doped α - Fe_2O_3 reached a maximum of 1.1 mA/cm² at 1.23 V vs. RHE, which increased approximately 3 times compared to that of pristine α - Fe_2O_3 . The excellent PEC activity could be attributed to Mg and Sn as structural directing agents relieving the lattice distortion, and improving both the charge injection efficiency and charge separation efficiency without obviously changing the carrier concentration, which was proved by electrochemical impedance spectroscopy (EIS)^[57].

As we summarized above examples about hematite doping, regardless of n-type metal/non-transition metal doping, or mono-doping/multi-doping, these doping attempts are aim to modify the intrinsically limited conduction property of hematite^[13]. However, it has been recently found that Ti^{4+} could act as electron-hole recombination centers in hemat-

ite due to the formation of Ti surface sites. On the other hand, it has been reported that Ti^{4+} surface species of Ti doped hematite may capture and store its holes, and promote them transfer to the electrolyte for water oxidation^[58]. Therefore, further investigations on the especial effect of dopants on the charge separation and transfer property of hematite are imperative.

3.3. Surface modification for charge separation

Besides doping and nanostructure engineering strategies, surface modification is also an effectual method for the improvement of the charge separation and transfer of hematite^[23, 59, 60]. Proper oxygen evolution catalysts or noncatalytic passivation layers coupling have been demonstrated to have effective improvement in the PEC water oxidation performance of hematite photoanodes, as shown in Fig. 6. In theory, when the photogenerated holes of hematite photoanode react with water molecules rapidly, the accumulation of holes on the surface of hematite would be avoided resulting in the suppression of hematite's photocorrosion, and thus its PEC water oxidation activity will be further enhanced^[61]. Since the oxygen evolution catalysts have catalytic activity for water oxidation^[62], the water oxidation overpotential of hematite photoanodes could be reduced through the co-catalysis. In addition, the presence of passivation layers on hematite can reduce its surface defects that induce the recombination of holes-electrons, thus surface passivation has similar ef-

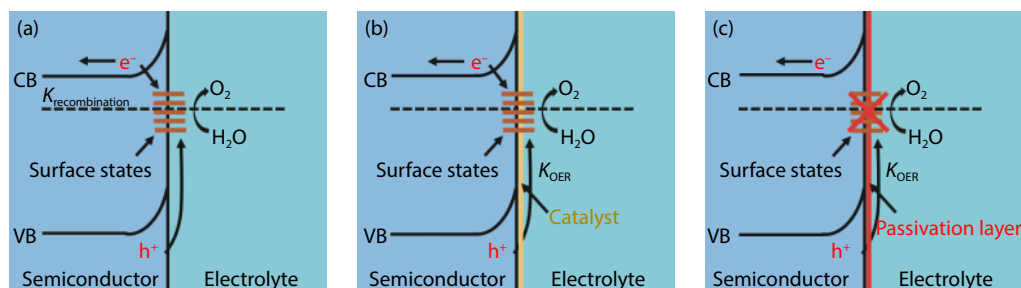


Fig. 6. (Color online) Comparison of the band structure of an n-type semiconductor photoanode in the presence and the absence of passivation layers inside a PEC cell. (a) High charge recombination at surface defects and inefficient water oxidation by the photogenerated holes. (b) Use of an OER catalyst layer, which promotes facile hole transfer across the interface to the electrolyte for improving water oxidation. (c) Use of thin non-catalytic passivation layers which suppress surface recombination and improve water oxidation.

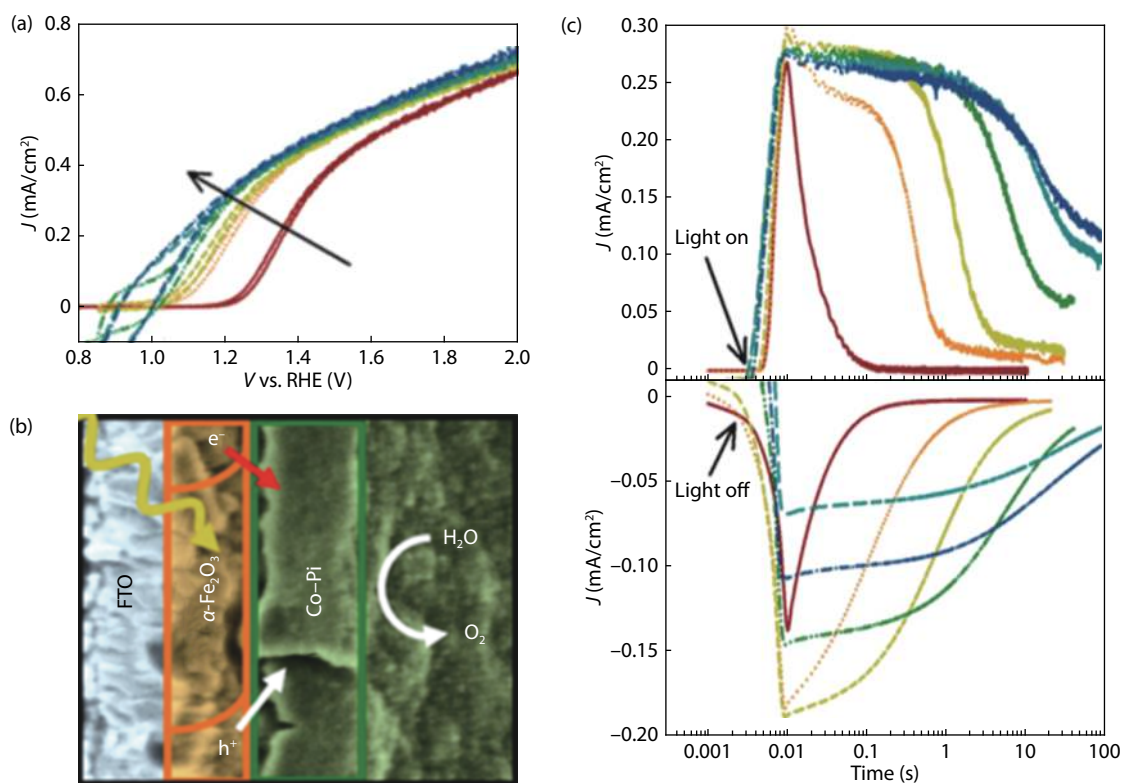


Fig. 7. (Color online) (a) J - V curves of a bare hematite electrode (red solid line) and the same electrode after depositing 1 (orange dotted line), 2 (yellow short dashed line), 15 (green dashed double dotted line), 45 (teal long dashed line), and 90 (blue dashed single dotted line) mC/cm^2 Co-Pi catalyst at 5 mV/s . (b) Proposed mechanism of the catalytic process. (c) Anodic and cathodic transient currents at an applied bias of 1.05 V vs. RHE. Reproduced from Ref. [63].

fect to oxygen evolution catalysts coupling. Furthermore, surface chemical corrosion also can improve the charge separation efficiency of hematite by changing its surface chemical states. In this section, co-catalysts, surface chemical corrosion and passivation layers which have been recently developed for the modifications of hematite photoanodes will be reviewed.

3.3.1. Cocatalyst

To modify the charge separation and injection of hematite photoanodes, various cocatalysts have been loaded on the hematite to improve its surface reaction kinetics for water oxidation. Typical OER cocatalysts are noble catalysts (such as, Pt, Ru) and metal oxides (such as, IrO_2 , RuO_2). Even though the noble metal-based cocatalysts are efficient and stable under working conditions, there are not suitable to

large-scale application in PEC devices owing to their high-cost and rarity. Therefore, cobalt-based and nickel-based compounds, chalcogenides have been developed as noble metal-free cocatalysts for the surface modification of hematite photoanode based on their high catalytic activity of water oxidation, low-cost and low-toxicity.

Among the noble metal-free cocatalysts, the typical compounds are cobalt oxides and amorphous cobalt-phosphate (Co-Pi)[63, 64]. For instance, Hamann *et al.* reported that the Co-Pi coupled hematite has high anodic current in charging under transient irradiation as well as high cathodic current in discharge when the irradiation disappearing[65]. It is demonstrated that the Co-Pi could collect the surface holes of hematite photoanode and improve its water oxidation performance (as shown in Figs. 7(a)–7(c)). Another typical example is

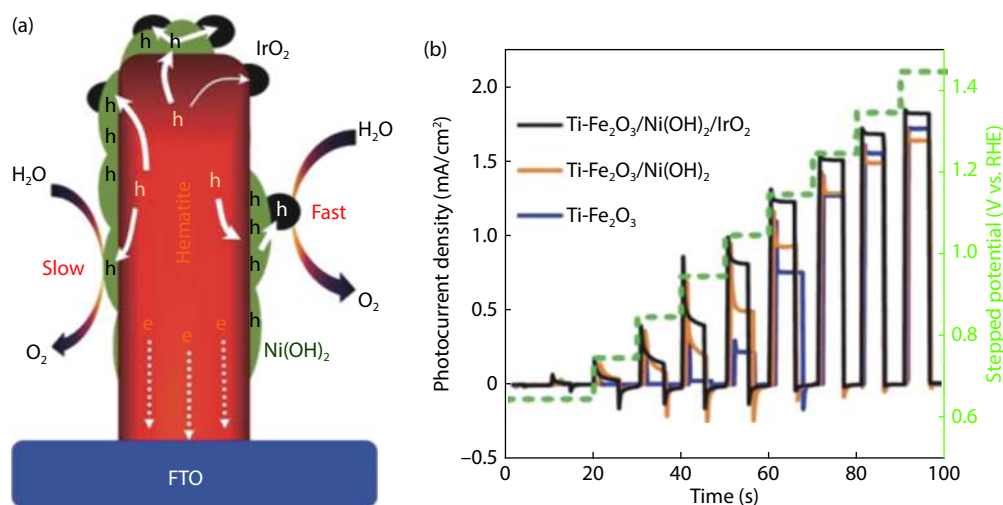


Fig. 8. (Color online) (a) Scheme of charge transfer from Fe_2O_3 to H_2O through $\text{Ni}(\text{OH})_2$ and/or IrO_2 . (b) Chronoamperometry measurement of $\text{Ti-Fe}_2\text{O}_3$, $\text{Ti-Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2$, and $\text{Ti-Fe}_2\text{O}_3/\text{Ni}(\text{OH})_2/\text{IrO}_2$ under a stepped potential. Reproduced from Ref. [20].

that the onset potential of hematite photoanode was shifted to 0.50 V after the amorphous Co-Pi decorating on its surface owing to reduce its the water oxidation overpotential through Co-Pi co-catalysis^[66]. Furthermore, based in the fact of Co-Pi boosting the photocurrent onset potential of hematite photoanodes, the electrocatalytic activity of Co-Pi for water oxidation reaction is further explored. The investigation of the Co-Pi/hematite photoelectrode found high-valent Co(IV)-O intermediates could be firstly formed in Co-Pi and these actives can “store” up the holes of hematite to achieve the water oxidation more effective, then the Co^{II} species be generated after the evolution of O_2 ^[21, 63, 67–69]. Although loaded Co-Pi electrocatalyst can obviously improve the PEC performance of hematite photoanode, optimal electrocatalyst has its own deficiencies, for instance, the question of Co-Pi catalyst resulting in light loss. Aiming at the question of Co-Pi catalyst, an ultrathin cobalt oxide layers (e.g. Co_3O_4 , $\text{Co}(\text{OH})_2$) load on surface of hematite by atomic layer deposition to enhance the charge separation efficiency^[70, 71]. These foregoing discussion illustrate that the addition of cobalt oxides/hydroxides layers is of proven benefit to facilitate electron hole separation of hematite electrodes, but their exact mechanism has not yet been clearly revealed by far.

In recent years, Ni-based catalysts, such as NiOOH , Ni-Bi, and Ni-Co double hydroxides, have also been investigated to enhance the surface activity of hematite photoanodes. Kelley *et al.* reported $\text{NiO}/\alpha\text{-Fe}_2\text{O}_3$ electrodes for PEC water splitting using atomic layer deposition method for the preparation of NiO. Compared to the untreated $\alpha\text{-Fe}_2\text{O}_3$, they found that the as-deposited NiO on $\alpha\text{-Fe}_2\text{O}_3$ could be converted into $\text{Ni}(\text{OH})_2$ during PEC water oxidation conditions, which resulted in the photocurrent onset potential of $\alpha\text{-Fe}_2\text{O}_3$ decreased by 300 mV and the photocurrent density increased by 200% at 1.23 V vs. RHE^[72]. Additionally, the PEC water oxidation activity of hematite photoanodes can also be enhanced by Ni-Bi^[73], or NiOOH ^[18]. Substantially, the enhanced PEC performance of hematite is attributed to a two-step process of Ni(II) catalysts for hematite water oxidation. The first step is the fast oxidation of Ni^{2+} into Ni^{3+} , then is the slow oxidation of Ni^{3+} into Ni^{4+} . The Ni^{4+} is deemed to be the active species^[74], which could accelerate the kinetics of holes-transfer to electro-

lyte, reduce the accumulation of holes at the photoanode/interface, and thus improving water oxidation performance of hematite. Apart from the single catalysts, the double catalysts have also been studied to the modification of hematite photoanodes owing to their low cost and promising catalytic activities. Recently, Wang *et al.* found Ni-based complex combining with Ir-based complex has the synergistic effect that the Ni-based complex acts the holes-transfer pathway and holes-storage layer, and the Ir-based complex works as catalyst for water oxidation. For example, higher photocurrent and better stability were observed on the Fe_2O_3 photoanode for water oxidation after modified by conjunct $\text{IrO}_x/\text{Ni}(\text{OH})_2$ relative to the bare Fe_2O_3 photoanode (Fig. 8)^[20]. For this $\text{IrO}_x/\text{Ni}(\text{OH})_2/\text{Fe}_2\text{O}_3$ photoanode, $\text{Ni}(\text{OH})_2$ is the holes-transfer pathway and holes-storage layer, IrO_x is the catalyst for water oxidation. Most recently, Du *et al.* demonstrate that a non-stoichiometric nickel-cobalt double hydroxide can achieve overall water splitting by itself upon solar light irradiation, avoiding the consumption of noble metal co-catalysts. This work is the first report on driving overall water splitting with a single-phase hydroxide, and thus represents a breakthrough in the direct conversion of solar energy into a hydrogen source^[75].

Besides Co-, and Ni-based catalysts possess high activity to OER, several other catalysts (e.g., FeOOH ^[76, 77], Ni-Fe LDH^[78], and NiFeO_x ^[79]) also have been used in combination with hematite for PEC water oxidation. Particularly relevant work is that amorphous NiFeO_x catalyst medicated hematite photoanode, an unprecedented water oxidation photocurrent onset was obtained compared with the hematite photoanode coupled with Co-Pi and NiO_x -cocatalyst owing to the enhancement in interface energetics^[68]. Our group developed an $\text{FeB}/\text{Fe}_2\text{O}_3$ -nanorod photoanode through dipping Fe_2O_3 into NaBH_4 solution at room temperature (Fig. 9(a)). The FeB-coupled hematite photoanode has a two-fold increment in water oxidation photocurrent and an obviously decreased onset potential relative to the bare Fe_2O_3 photoanode. Since the FeB can work as efficient catalyst to suppress charge recombination of Fe_2O_3 and decrease the Fe_2O_3 /electrolyte interface resistance, the charge separation and transfer efficiency of Fe_2O_3 photoanode were significantly improved (as shown

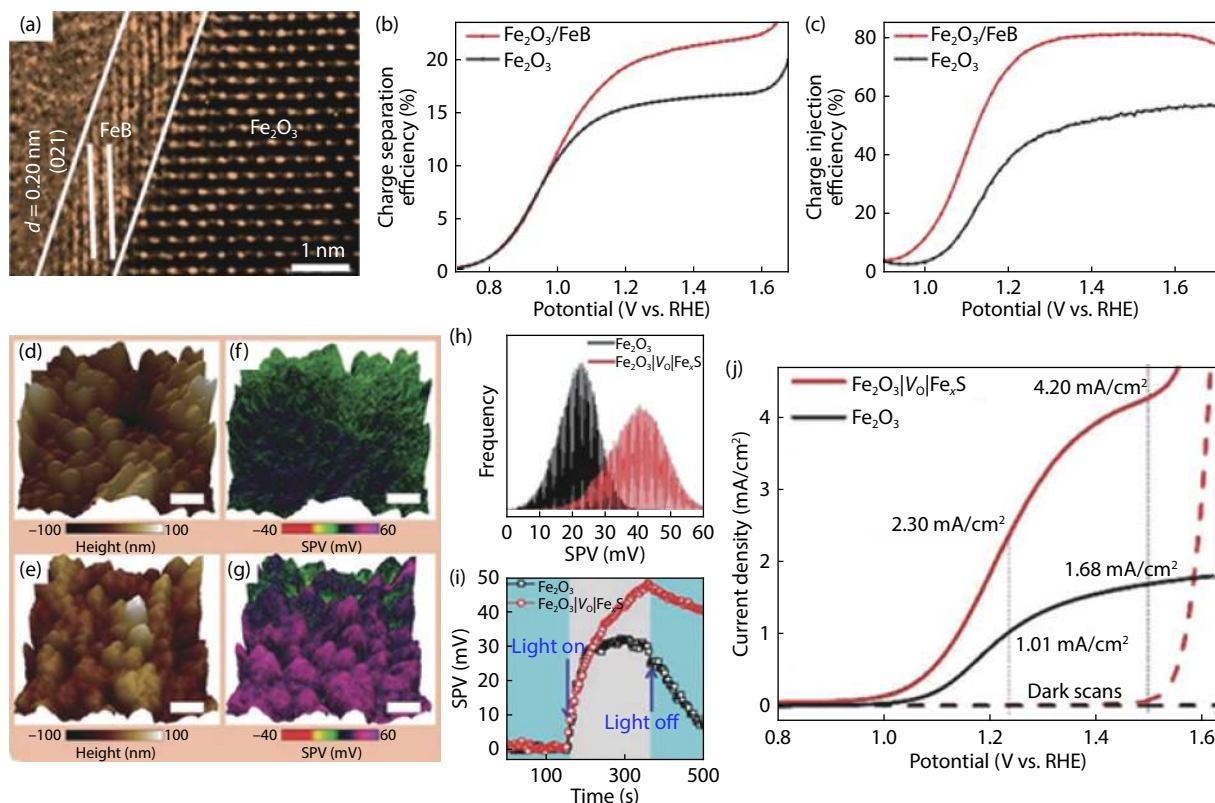


Fig. 9. (Color online) (a) High-resolution TEM images of $\text{Fe}_2\text{O}_3/\text{FeB}$ photoanode. (b) Charge separation and (c) injection efficiency at 1.23 V vs. RHE for the Fe_2O_3 and $\text{Fe}_2\text{O}_3/\text{FeB}$ photoanodes. Reproduced from Ref. [80]. (d, e) AFM images and (f, g) the corresponding SPVM images of (d, f) Fe_2O_3 and (e, g) $\text{Fe}_2\text{O}_3|\text{V}_0|\text{Fe}_x\text{S}$, respectively. Scale bars in (a–d), 200 nm. (h) Histograms of the SPV distributions on the Fe_2O_3 and $\text{Fe}_2\text{O}_3|\text{V}_0|\text{Fe}_x\text{S}$ electrodes. (i) Time evolution of SPV generation and decay with light on and off on Fe_2O_3 and $\text{Fe}_2\text{O}_3|\text{V}_0|\text{Fe}_x\text{S}$. All the SPV signals are obtained under 450 nm laser illumination at a light intensity of $4 \text{ mW}/\text{cm}^2$. (j) Photocurrent-potential (J - V) curves of the Fe_2O_3 and $\text{Fe}_2\text{O}_3|\text{V}_0|\text{Fe}_x\text{S}$ photoanodes in a 1 M NaOH (pH ~ 13.6) aqueous electrolyte under AM 1.5G illumination and in the dark. Reproduced from Ref. [81].

in Figs. 9(b) and 9(c)[80]. In addition, $\text{Fe}_x\text{S}/\text{Fe}_2\text{O}_3$ photoanode was also prepared by our group to boost the water oxidation activity of Fe_2O_3 photoanodes by the partial sulfurization of Fe_2O_3 . The Fe_xS -modified Fe_2O_3 photoanode exhibited a higher and stabler photocurrent of $2.30 \text{ mA}/\text{cm}^2$ at 1.23 V vs. RHE, and a saturated photocurrent of $4.20 \text{ mA}/\text{cm}^2$ at 1.50 V vs. RHE (as shown in Fig. 9(j)). From the investigation of *in situ* Kelvin probe force microscopy (KPFM) (Figs. 9(d)–9(i)), the enhanced PEC performance on the $\text{Fe}_x\text{S}/\text{Fe}_2\text{O}_3$ photoanode is attributed to that the presence of Fe_xS provides catalytic active sites, restrains the carrier recombination of Fe_2O_3 and promote its holes to participate in water oxidation[81]. It is obvious that the development of hematite PEC water splitting depends on the innovations on improving its charge separation and transfer, as well as promoting its surface catalysis by more efficient cocatalysts.

3.3.2. Surface passivation

Surface passivation is another efficient surface modification method to improve charge transfer and separation of hematite photoanode for solar water oxidation by removing unfavorable surface states of semiconductor, which often act as recombination centers competing intensively with charge transfer from the semiconductor to the electrolyte. Since some researchers had discovered surface states are located at just slightly positive than water oxidation potential (1.23 V vs. RHE) but more negative than valence band with two measures in neutral and basic conditions[23]. In this context, holes

that generated in hematite should be more inclined to first transfer to those surface states then to water. In other word, surface states trap hole carriers, leading to recombination of electron hole pairs for indirect charge transfer to water oxidation reaction. Based on it, we will here highlight surface states mediated charge transfer mechanism for PEC water oxidation. Hamann *et al.* found after hematite annealing at 800°C the water oxidation efficiency of the ultrathin film hematite electrodes substantially is improved since the removal of the surface states/mid-gap states close to the conduction band of the hematite photoanodes and the reduction in recombination and Fermi level pinning[82]. Additionally, Li *et al.* put forward another mechanism view using a simple acid treatment method amended position of the available trap sites, which substantially boosts electrons moving out of traps in hematite nanowire photoanodes, and thus reduces the electron hole pairs recombination loss and improves PEC performance[83]. Analogously, Kim *et al.* reported that upon phosphate-based solution treatment of hematite, the negatively charged PO_3^{4-} ions attached to the $\alpha\text{-Fe}_2\text{O}_3$ surface promoted hole extraction and injection from the photoanode into the electrolyte, thus increasing the electron hole pairs separation in hematite and leading to a three-time higher photocurrent density than that measured with the bare oxide[84]. Furthermore, introducing an very thin passivating layers on surface of hematite also can enhance the charge separation and suppress the recombination due to either shield surface

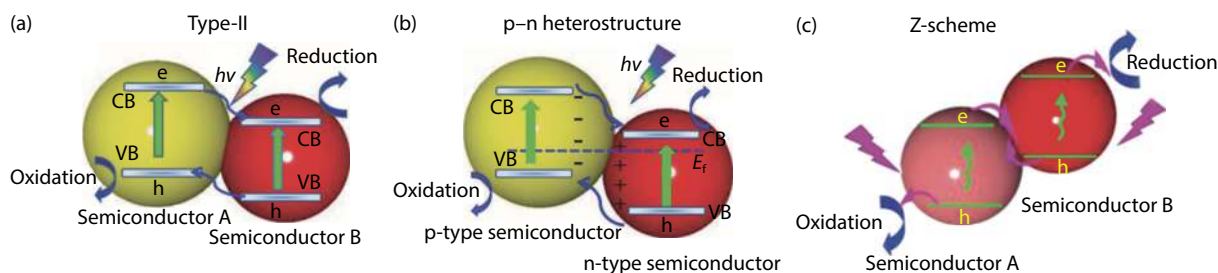


Fig. 10. (Color online) Schematic illustration of (a) the type-II heterostructure, (b) p-n heterostructure, and (c) Z-scheme system without electron-mediators band alignments, and the correspondingly possible separation and transfer process of photoinduced electron-hole pairs of semiconductor photocatalysts. Reproduced from Refs. [92, 93].

states from contact with water or just simply eliminate surface states to facilitate direct the valence band to electrolyte injection^[85–89]. For passivating layers relatively insulating ultrathin metal oxide or semiconductor coating with wide band gap (ALD TiO_2 , ALD Al_2O_3 , and Ga_2O_3 etc^[89, 90]) have been explored. For example, the effect of a sub-monolayer of atomic layer deposition TiO_2 deposited on hematite on the surface states were studied with photoelectron spectroscopy, transient absorption spectroscopy, and electrochemical impedance spectroscopy, and found a second intermediate surface state and passivation of the recombination surface states^[91]. Le Formal *et al.* also using electrochemical impedance and photoluminescence spectroscopy found that after the Al_2O_3 overlayer modified on surface of Fe_2O_3 , a significant change in the surface capacitance and radiative recombination, respectively, which revealed an ultra-thin coating of Al_2O_3 faster charge carrier dynamics resulting from passivation of surface states, and then resulting in the increased photoelectrochemical performance^[90]. Although these previous studies have reported surface states mediated charge transfer several mechanisms, great efforts are still required to further explore charge transfer efficiency of hematite based photoanodes for PEC water oxidation.

3.4. Building heterojunctions for charge transport and separation

Building heterojunctions is also one of the most common strategies to tackle the rapid bulk charge recombination and thus to increase PEC performance by increasing the charge spatial separation. So far, the models of heterojunction primarily include conventional type-II heterojunction, p-n heterojunction, Z-scheme photocatalytic system, semiconductor-metal heterojunction, and so on (as depicted schematically in Fig. 10). The four different heterojunctions have various mechanisms on enhancing charge separation which mainly depend on the electronic properties of the partner materials. For conventional type-II heterostructure, the conduction band (CB) and the valence band (VB) levels of semiconductor A are higher than the corresponding levels of the semiconductor B. Thus, the photogenerated electrons will transfer to semiconductor B, while the photogenerated holes will migrate to semiconductor A under light irradiation, resulting in a spatial separation of electron-hole pairs. For p-n heterojunctions, an additional internal electric field form at the heterojunction interface which lead to a band bending compared to conventional type-II heterostructure, electrons have a tendency to flow from the higher to the lower lying conduc-

tion band, while holes will follow the opposite direction. For Z-scheme photocatalytic systems, the photo-induced electrons on the semiconductor with a lower CB potential will combine with the holes on another semiconductor with a higher VB potential, and leave the electrons and holes persevere of the strong redox ability in reduction evolving and oxidation-evolving semiconductors, respectively, thus leading to superior charge separation. For semiconductor-metal type heterojunction, the Schottky barrier which is obtained by interfacial a semiconductor with a metal, is employed to drive electron moving from the material with the higher Fermi level to that with a lower one, until steady-state equilibrium is reached.

The conventional type-II and p-n heterojunction are common configuration to facilitate charge separation and transfer as well as the promotion of PEC water splitting performance due to their band matching effect or the formation of additional electric field at the interface of p-n junction. Various hematite-based heterojunction photoelectrode structures such as $\text{TiO}_2/\text{Fe}_2\text{O}_3$, $\text{WO}_3/\text{Fe}_2\text{O}_3$, $\text{MgFe}_2\text{O}_4/\text{Fe}_2\text{O}_3$, and $\text{Fe}_2\text{O}_3/\text{BiVO}_4$, etc^[94–99] have been shown to enhance the PEC performance of the hematite photoanode. Special representative work is that Miao's group independently reported $\text{Fe}_2\text{O}_3/\text{ZnFe}_2\text{O}_4$ heterojunction photoanodes that exhibit a significantly enhanced photocurrent response compared to the bare Fe_2O_3 electrode^[100]. The enhanced electron-hole separation was stemmed from the conduction and valence band edge position of ZnFe_2O_4 situated at ca. 200 mV negative from that of Fe_2O_3 . In a separate study, the photocurrent of $\text{SrTiO}_3/\text{Fe}_2\text{O}_3$ heterojunction photoanode is higher than single SrTiO_3 or Fe_2O_3 since the electric field formed by the junction at the interface and the special band structures of SrTiO_3 that favor the transfer of holes from Fe_2O_3 to SrTiO_3 , and the improved charge separation at the $\text{SrTiO}_3/\text{Fe}_2\text{O}_3$ interface^[101]. Furthermore, a $\text{NiO}/\text{Fe}_2\text{O}_3$ p-n heterojunctions was fabricated by depositing p-type NiO nanoparticles on the Fe_2O_3 thin film. The highlight of using this approach to prepare $\text{NiO}/\text{Fe}_2\text{O}_3$ electrode is the dual effect of NiO for separation of electrons and holes via the p-n junction, and the use of NiO as an efficient hole acceptor which reduced the overpotential for water oxidation^[102, 103].

From charge transfer mechanism of the aforementioned two-types heterojunction standpoint, although the conventional type-II and p-n heterojunctions make the photogenerated electrons and holes spatially isolate, which greatly inhibits their undesirable recombination, the disadvantage is that the redox ability of photogenerated electrons and holes is

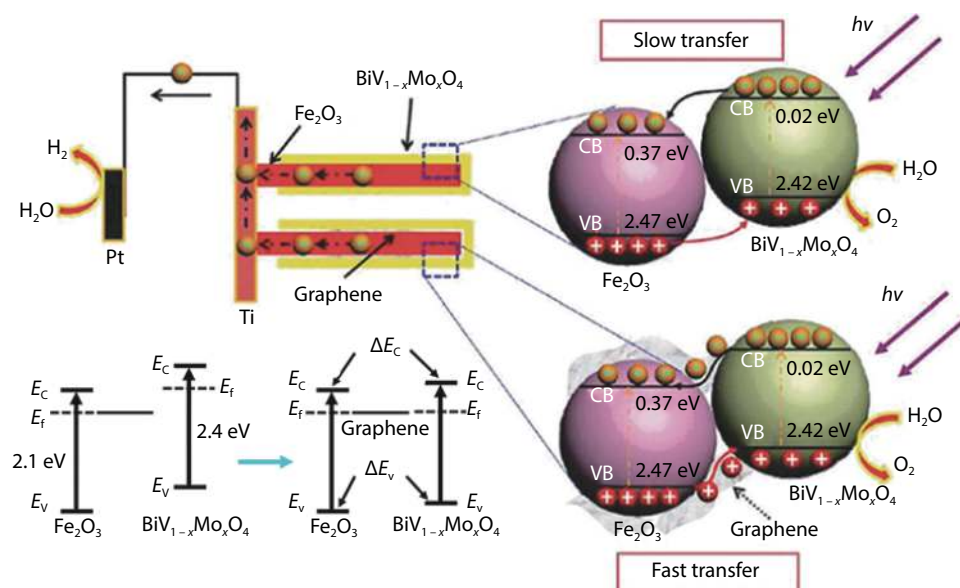


Fig. 11. (Color online) Schematic for the energy band structure of the Fe_2O_3 -NA/RGO/ $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ heterojunction and the proposed mechanism of PEC water splitting. Reproduced from Ref. [105].

weakened after charge transfer because the VB potential of semiconductor A is less positive than that of semiconductor B and the CB potential of semiconductor A is less negative than that of semiconductor B. Hence, it is difficult for the present heterojunction-type photocatalytic system to simultaneously possess the high charge-separation efficiency and strong redox ability. Thus, the development of a new-type photocatalytic system is urgently needed to solve the aforementioned problems.

The artificial Z-scheme photocatalytic system have attracted an ever-growing number of scientists to this field since the concept of "Z-scheme" is proposed by Bard *et al.* in 1979^[104], because the Z-scheme photocatalytic system not only features the spatial isolation of photogenerated electrons and holes, which reduces the bulk electron-hole recombination, but also maximizes the redox potential of the heterojunction systems. In the past decades, many studies have been published on the development of Z-scheme photocatalytic system for water splitting. For example, the PEC activity of $\alpha\text{-Fe}_2\text{O}_3$ nanorod/graphene/ $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ core/shell heterojunction arrays photoelectrodes are enhanced due to the band potential differences between $\alpha\text{-Fe}_2\text{O}_3$ nanorod and $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$. Meanwhile, the RGO sheets could act as quick paths for the electrons that are transferred from the $\text{BiV}_{1-x}\text{Mo}_x\text{O}_4$ shell to the Fe_2O_3 core (Fig. 11)^[105]. In our recent work, a novel $\text{Sb}_2\text{Se}_3/\text{Fe}_2\text{O}_3$ electron mediator-free Z-scheme system was synthesized by means of chemical vapor deposition. The all-solid-state Z-scheme $\text{Sb}_2\text{Se}_3/\text{Fe}_2\text{O}_3$ achieved a high photocurrent density of 3.03 mA/cm^2 at 1.23 V vs. RHE under simulated sunlight, and showed a cathodic shift of about 200 mV in onset potential. The improved PEC activity is attributed to the unique mechanism of charge separation and transfer, in which the photogenerated electrons in the conduction band of Fe_2O_3 and the photogenerated holes in the valence band of Sb_2Se_3 recombine rapidly. As a result, the photogenerated electrons in conduction band of the Sb_2Se_3 migrate to electron collection substrate, while the photogenerated holes allow a high concentration and persever-

ing with strong oxidation ability in valence band of Fe_2O_3 are collected for water oxidation^[106].

Other hematite-based heterojunctions were combined with nanocarbons as an electron conducting scaffold, such as reduced graphene oxide^[107, 108], graphene^[109], carbon nanotubes^[110], and carbon quantum dots^[111], to enhance its poor charge separation efficiency through utilizing nanocarbons' unique physicochemical, electronic and optoelectronic properties^[112, 113]. Interestingly, in most of these studies, Kim and coworkers published a report on Fe_2O_3 photoanode modified with carbon nanotubes (CNTs), and after modification the photocurrent of samples exhibited 66% increment compared to the unmodified Fe_2O_3 electrode^[114]. Through EIS investigations, they observed that the presence of CNT obviously reduces the resistance over the entire electrode and increases capacitance at the interface between CNTs and the conducting substrate, suggesting an increased electron passage from the hematite to the conductive oxide substrate. In addition, coupling of $\alpha\text{-Fe}_2\text{O}_3$ to graphene nanoplates of 0.2 wt.% allowed for efficient water oxidation, and the photocurrent of 2.5 mA/cm^2 at 0.75 V vs. saturated calomel electrode (SCE) was achieved under visible light irradiation due to efficient charge transfer at the semiconductor/electrolyte junction, a red shift in the absorption spectra of the Fe_2O_3 -graphene nanoplates compared to pristine $\alpha\text{-Fe}_2\text{O}_3$, and improved conductivity of $\alpha\text{-Fe}_2\text{O}_3$ because of the introduction of conductive graphene^[115]. In addition to nanocarbons-hematite composite nanostructures, specially, coupling $\alpha\text{-Fe}_2\text{O}_3$ with other metals/metallic species can improve the conductivity and transfer of electrons to the counter electrode using the conductive and surface area advantages of metallic species on charge collecting. In the work of Wang's group, $\alpha\text{-Fe}_2\text{O}_3/\text{TiSi}_2$ nanonet with core-shell heterojunction was synthesized and investigated as photoanode for solar water splitting^[116]. The connectivity of $\alpha\text{-Fe}_2\text{O}_3/\text{TiSi}_2$ provides heterojunction interface for charge transport, and thus better PEC water splitting performance is obtained on the $\alpha\text{-Fe}_2\text{O}_3/\text{TiSi}_2$ photoanode relative to the pristine $\alpha\text{-Fe}_2\text{O}_3$ (Fig. 12).

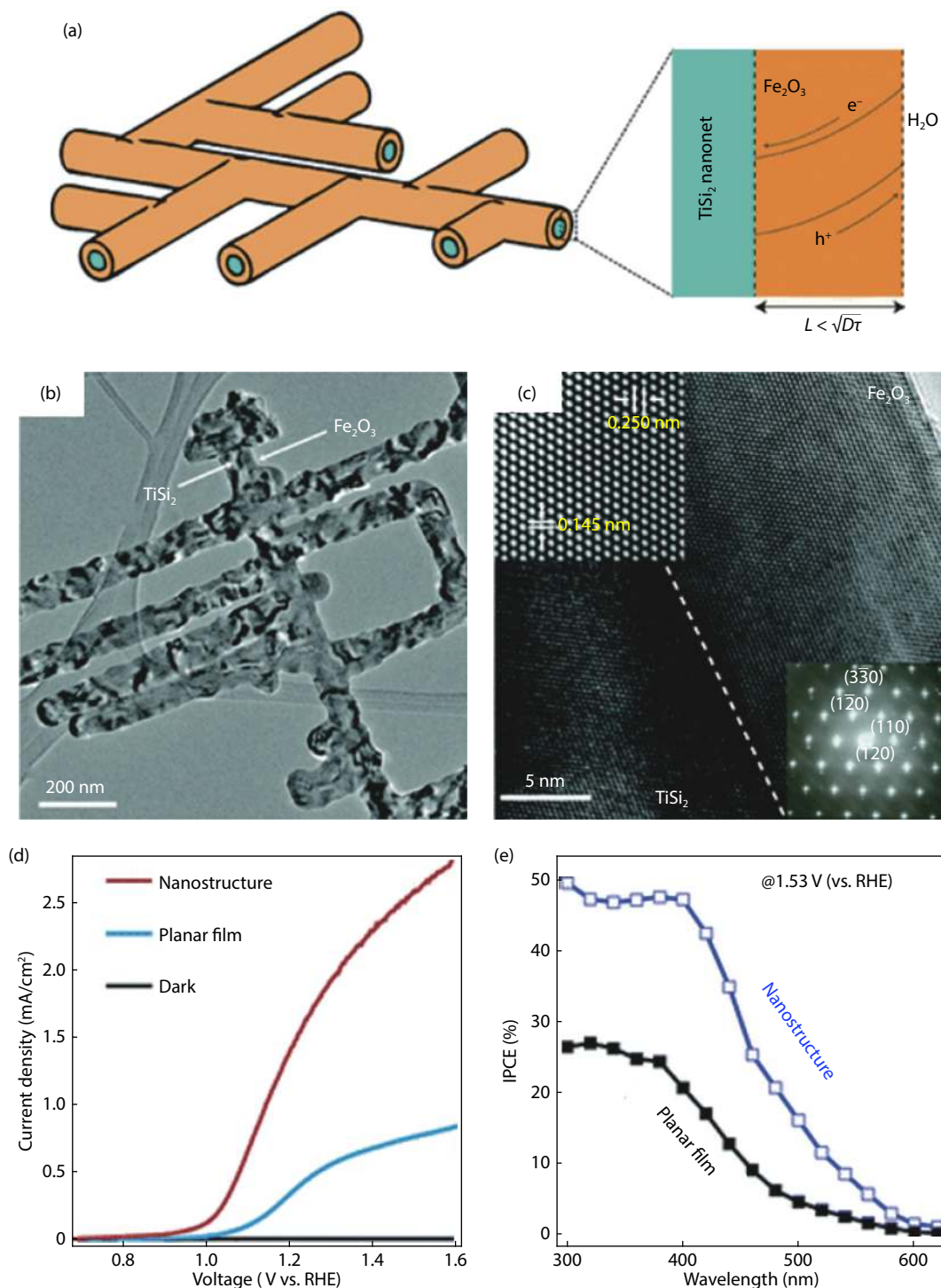


Fig. 12. (Color online) (a) TiSi_2 nanonet-based hematite nanostructure is essentially a core/shell arrangement where the core is the nanonet for effective charge collection and the shell is hematite for photocatalytic functionalities. The electronic band structure is shown in the enlarged cross-sectional view. (b) Low- and (c) high-magnification transmission electron microscopy (TEM) images showing the conformal coverage and crystallinity of hematite. (d) J - V curves of an $\text{Fe}_2\text{O}_3/\text{TiSi}_2$ heteronanostructure and a planar hematite film. (e) IPCE comparison of Fe_2O_3 with and without TiSi_2 nanonets. Reproduced from Ref. [116].

As discussed above, one strategy fabricating heterojunction structures can enhance charge separation and transfer of electrodes. The main idea of heterojunction is to use electronic properties of additional material components to improve charge separation. So, further development of new materials for the design and fabrication of high-quality hematite-based heterojunction is one of the key research goals. Moreover, although Z-scheme photocatalytic system is more beneficial to spatially separate the electrons–holes due to its unique

charge separation and transfer mechanism than other heterojunctions (e.g., conventional type-II heterojunction, and p–n heterojunction, etc.), the transfer pathway of photogenerated charge at the heterojunction interface and charge-migration kinetics in the Z-scheme heterojunction do not achieve a deeper understanding. Therefore, further investigation of these issues is important for confirming the formation of different types of heterojunction photocatalysts, and further advancements in theoretical calculations are highly desirable to

shed some light on the true picture of the photocatalytic processes in the heterojunction photocatalysts.

4. Other strategies

Apart from above mentioned strategies, there are several other approaches have been reported to modify the hematite photoanode for solar water oxidation. Itoh, Liang and Bockris *et al.* have approved that the poor water oxidation activity of hematite photoanode depends on the enhanced bulk recombination that induced by the hematite/FTO substrate interface effect^[117–119]. Therefore, a connecting layer introduced between the hematite and charge collector can reduce the charge recombination at the back of hematite photoanode. To facilitate the charge separation in hematite photoanode, several explorations have been conducted through the introduction of metal oxide underlayers on the FTO substrate. Hisatomi *et al.* reported when Nb₂O₅ underlayers deposited directly on FTO, the PEC activity of ultra-thin hematite can be improved, since the lower conductivity of Nb₂O₅ underlayer could suppress the back injection of electrons^[117]. Similar result was found in the work of Wang *et al.*^[120], they introduced TiO₂ underlayer between the FTO and hematite to suppress its charge recombination. Additionally, we have observed that the Ti⁴⁺ doped hematite after surface corrosion with hydrochloric acid has 100 mV cathodic shift in the photocurrent onset potential, owing to the suppression of back reaction of electrons^[121].

In addition, hematite-cocatalyst interface engineering is also a critical method for boosting the charge transfer from hematite to cocatalyst. In this approach, the cocatalysts usually coupled with other interlayers (such as hole-transport, hole-storage, electron-blocking layer), and the activity and stability of hematite photoanode can be obviously improved by the resultant interface engineering. For example, Ni-based complex could act as a holes-storage layer, and Ir-based complex could work as an OER catalyst, thus significantly enhanced photocurrent is achieved on the Ir-based complex/Ni-based complex/hematite photoanode^[20]. Moreover, based on the plasmonic property of nanostructured Au and Ag, integrating hematite with plasmonic nanostructures has demonstrated to be functional way to enhance its charge separation efficiency. This enhancement is attributed to the local surface plasmon resonance (LSPR) effects of plasmonic nanostructures have function of improving the charge separation of hematite photoanode^[98, 122, 123].

5. Summary and Perspectives

In summary, the strategies developed for the modification of charge separation and transfer of hematite photoanode were summarized in the present review to help readers to get insight into the modifications progress for metal oxide photoanodes. The advantages and limitations of hematite photoanode for solar water splitting were firstly presented. Based on their function of improving hematite photoanode performance for solar water oxidation, several typical strategies including of nanostructuring, doping, surface modification and junction building are systematically categorized and introduced.

PEC water splitting is a promising pathway to produce hydrogen fuel using solar energy. Although the solar-to-fuel efficiency of PEC water splitting still some way off the require-

ments of commercialization, the progress in the hematite photoanode in the last ten years is heartening. In our opinion, the following research directions are important to develop high performance hematite photoanode. (1) The development of effective combination of experimental investigation and theoretical simulation to understand the charge separation and transfer in modified hematite photoanodes. (2) The systematical investigation of water oxidation mechanism on hematite photoanodes to guide developing new modification methods.

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