

Hematite Photoanodes Decorated with a Zn-doped Fe₂O₃ Catalyst for Efficient Photoelectrochemical Water Oxidation

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Hematite is considered to be an attractive photoanode material for photoelectrochemical (PEC) water oxidation. Its application is limited by several inherent deficiencies, such as low conductivity, severe surface recombination and sluggish oxygen evolution kinetics. Numerous oxygen evolution reaction (OER) electrocatalysts have been explored to enhance the PEC properties of hematite photoanodes. Herein, an Fe-based OER catalyst, namely, Zn-doped Fe₂O₃, was deposited on the surface of hematite by a facile spin-coating method. Compared with bare hematite, all the surface-modified samples negatively shifted the onset potential by approximately 100 mV, and the photocurrent increased rapidly in a linear dependence on the bias. Electrochemical impedance, Mott-Schottky, separation and injection efficiency measurements were conducted to elucidate the mechanism for the enhancement. Several other tactics, such as phosphorus doping and passivation layer deposition, have been incorporated to increase the photocurrent to 1.65 mA @1.23 V_{RHE} and 2.0 mA @1.4 V_{RHE}, indicating the presence of a synergistic effect between other strategies and the Zn-doped Fe₂O₃ catalyst.

Keywords: Hematite, Photocurrent, water splitting, Zn-doped Fe₂O₃, OER catalyst

1. INTRODUCTION

Hydrogen production from photoelectrochemical (PEC) water splitting is one of the most promising approaches to solve the energy crisis in an environmentally friendly way [1-5]. The activity and stability of photoanodes is a key factor in the PEC water oxidation process [6]. As a potential photoanode material, hematite has attracted much attention due to its narrow band gap (1.9~2.1 eV), high abundance, and low toxicity [2, 7]. However, several inherent deficiencies limit its application in PEC water oxidation, such as low conductivity [8, 9], severe surface recombination induced by surface states [10, 11] and slow oxygen evolution kinetics at the interface [12, 13]. In general, several strategies can be adopted to address the above issues, such as doping elements [8, 14-18], constructing heterojunctions [19, 20], applying passivation layers [21] and depositing cocatalysts [22-24]. Various

oxygen evolution reaction (OER) catalysts have been employed to enhance the PEC properties of hematite photoanodes, including traditional noble metal oxides such as IrO_2 [25], some amorphous phosphates such as Co-Pi [26, 27], transition-metal phosphides such as CoP [28], recently developed amorphous oxyhydroxides such as NiOOH [29, 30] and FeOOH [31], and oxides such as Co_3O_4 [32]. Among these compounds, amorphous oxyhydroxides have been developed recently and showed remarkable catalytic activity, especially FeOOH [31]. However, FeOOH has been reported to be oxidized easily to soluble FeO_4^{2-} in alkaline electrolytes during the electrocatalytic OER process [33, 34]. The authors also found that the reliability and repeatability of the FeOOH OER catalyst remain questionable when the OER catalyst is employed as a cocatalyst of photoanodes. Alternatively, earth-abundant transition metal oxides are ideal OER catalysts under alkaline conditions due to their excellent stability and low cost. Co_3O_4 has been extensively used as an electrocatalyst for electrocatalytic or PEC water oxidation [32, 35-37]. However, Fe_2O_3 is considered to be the worst OER catalyst among the transition metal oxides [38]. Normally, Fe_2O_3 can be used as a photoanode directly and decorated with OER catalysts.

Recently, powdered Zn-doped hematite was prepared by a combustion method and applied to electrodes for electrocatalytic OER [39]. Zn-doped hematite was found to exhibit superior catalytic performance for OER. A two-reaction center model has been proposed in which Zn facilitates a faster and thermodynamically favored alternative via a two-site reaction, where the four-electron oxidation reaction starts from Fe and is completed on Zn [39]. In this work, the *in situ* growth of Zn-doped Fe_2O_3 on the surface of hematite nanorods was attempted for the first time. Different amounts of Zn-doped hematite catalyst precursor were spin-coated on the hematite nanorod photoanodes, followed by annealing at various temperatures. The synergistic effect of the cocatalyst and passivation layers as well as bulk strategies toward PEC water oxidation on hematite were investigated.

2. EXPERIMENTAL SECTION

2.1 Photoanode preparation

(a) Preparation of bare hematite films

The bare hematite films were fabricated through a facile hydrothermal method [40]. In a typical process, 0.0972 g of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ and 0.034 g of NaNO_3 were dissolved in distilled water to form a 4-mL aqueous solution in a 10-ml beaker. Then, a clean fluorine-doped tin oxide (FTO) (F: SnO_2) glass was immersed into the solution with the conductive side downward leaning against the wall of the beaker. Then, the beaker was put into an oven and kept at 95 °C for 4 h. After cooling to room temperature, the FTO substrate with a uniform layer of FeOOH was removed, rinsed thoroughly with deionized (DI) water and dried with nitrogen. Then, the FeOOH film was annealed at 550 °C for 2 h and 750 °C for 15 min in air to give the bare hematite films.

(b) Preparation of cocatalyst-decorated hematite films

The cocatalyst-decorated hematite photoanodes were prepared through a spin-coating method

followed by combustion [39] at 200 °C. In a typical process, 1.114 g of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.0627 g of glycine were dissolved in 10 ml deionized water to give solution A. ZnCl_2 (0.0113 g) was dissolved in 60 ml DI water to give solution B. Two milliliters of solution A and 2 mL of solution B were removed and mixed homogeneously to give solution C with a Zn/Fe ratio of 3%. Then, a certain amount of solution C (60 μl , 120 μl , 240 μl) was removed and spin-coated on the surface of bare hematite with a rotation rate of 3000 rpm/min. Then, the photoanodes were transferred to a muffle oven and annealed at 200 °C for 2 hours in air. The resultant samples were named $\text{Fe}_2\text{O}_3/\text{Zn-Fe}_2\text{O}_3\text{-x}$ μl , where x represents the amount of solution C that was spin-coated on hematite, such as $\text{Fe}_2\text{O}_3/\text{Zn-Fe}_2\text{O}_3\text{-60}$ μl .

(c) Preparation of P-doped hematite films

Na_2HPO_4 (0.0355 g) was dissolved in 5 ml DI water to form solution A. The as-prepared FeOOH in section (A) was immersed in solution A for 1 min, transferred into a muffle furnace and annealed at 550 °C for 2 h and 750 °C for 15 min in air to give the P-doped hematite films, which can be referred to as p- Fe_2O_3 .

(d) Preparation of hematite films passivated by the FePO_4 layer

The FePO_4 passivation layer was formed by a low-temperature chemical vapor deposition method [41]. Typically, 0.024 g of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ was placed in the center of a quartz tube furnace. P-doped hematite films (p- Fe_2O_3) were placed in the position of the downstream side of the tube furnace, 10 cm away from the position of $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$. Then, the system was heated at 300 °C for 60 min in N_2 , followed by natural cooling to room temperature to give the surface-passivated samples, which can be referred to as p- $\text{Fe}_2\text{O}_3/\text{Fe-Pi}$.

(e) Preparation of hematite films with multiple modifications

A total of 120 μl of solution C (Section 2.21 (b)) was spin-coated on the surface of p- $\text{Fe}_2\text{O}_3/\text{Fe-Pi}$ with a rotation rate of 3000 rpm/min. Then, the photoanodes were transferred to a muffle oven and annealed at 200 °C for 2 hours in air. The resultant samples were named p- $\text{Fe}_2\text{O}_3/\text{Fe-Pi}/\text{Zn-Fe}_2\text{O}_3$.

2.2 Materials characterization

Scanning electron microscopy (SEM) was conducted on a JEOL/JSM7500 microscope coupled with an energy dispersive X-ray spectrometer. X-ray diffraction was performed on a Rigaku D/MAX-2500 powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15418$ nm). Elemental analysis was conducted by X-ray photoelectron spectroscopy (XPS) using an ESCALAB-MKII spectrometer (VG Co., UK). Ultraviolet-Visible (UV-Vis) absorption was measured by a UV-Visible spectrophotometer (Shimadzu, UV-2600).

The PEC performances of the photoanodes were evaluated on an electrochemical workstation (CHI660E) with a 300 W xenon lamp as the light source. The light power density in the position of the photoelectrode was adjusted to 100 mW cm^{-2} using an irradiance meter (Aulight). A three-electrode system was constructed with the hematite samples as the working electrode, platinum gage as the counter electrode, and an Ag/AgCl electrode as the reference electrode. A 1-M NaOH aqueous solution was used as the electrolyte. The exposed sample area was adjusted to be approximately 1 cm^2 using insulating tape. Electrochemical impedance spectroscopy (EIS) and Mott-Schottky (M-S) measurements of the hematite samples were performed with a Zennium electrochemical workstation (ZAHNER, Germany) using the same three-electrode system. M-S measurements were conducted at a frequency of 1 kHz in the dark. EIS measurements were carried out under light illumination at a potential of 0.05 V versus Ag/AgCl in a frequency range of 100 k - 0.1 Hz.

3. RESULTS AND DISCUSSION

3.1 PEC performance

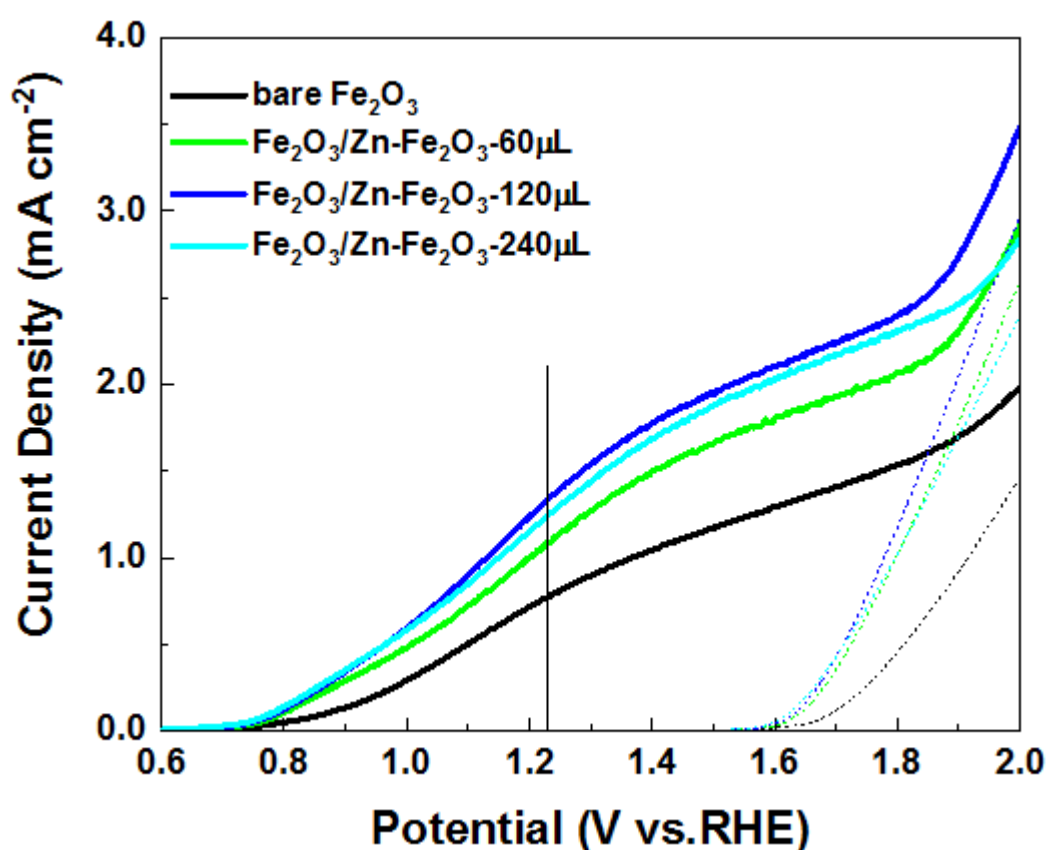


Figure 1. Current-voltage characteristic curves (J-Vs) of bare and surface-modified Fe_2O_3 with different amounts of catalyst recorded in illuminated (solid line) and dark conditions (dotted line)

The J-V characteristic plots of the bare and modified samples were recorded in 1-M NaOH solution in the dark (dashed line) and under illumination conditions (solid line). The photocurrent

density of the bare hematite rose from 0.8 V and increased gradually with increasing bias. There is a turning point at approximately 0.9 V_{RHE}, where the slope of the plot became steeper. Then, the slope reached 0.7 at 1.23 V_{RHE}. Compared with bare hematite, all the surface-modified samples negatively shifted the onset potential by approximately 100 mV. Then, the photocurrent increased rapidly in a linear dependence on the bias and reached a plateau at approximately 1.4 V_{RHE}. The initial slope is larger than the slope of the bare hematite, indicating a higher reaction rate and lower apparent resistance. For the modified hematite, the profiles of the *J-V* plots were different due to varied amounts of decoration. The intermediate amount (120 μ L) outperformed with the highest photocurrent density of 1.34 @ 1.23 V_{RHE}. Usually, the onset potential for the dark current can offer useful information about the catalytic effect [42]. The dark currents of all the modified hematite films showed a distinct cathodic shift for the onset potential, indicating that the surface modified with Zn-doped hematite had an apparent electrocatalytic effect for the oxygen evolution reaction [15, 42].

3.2 Structure characterization

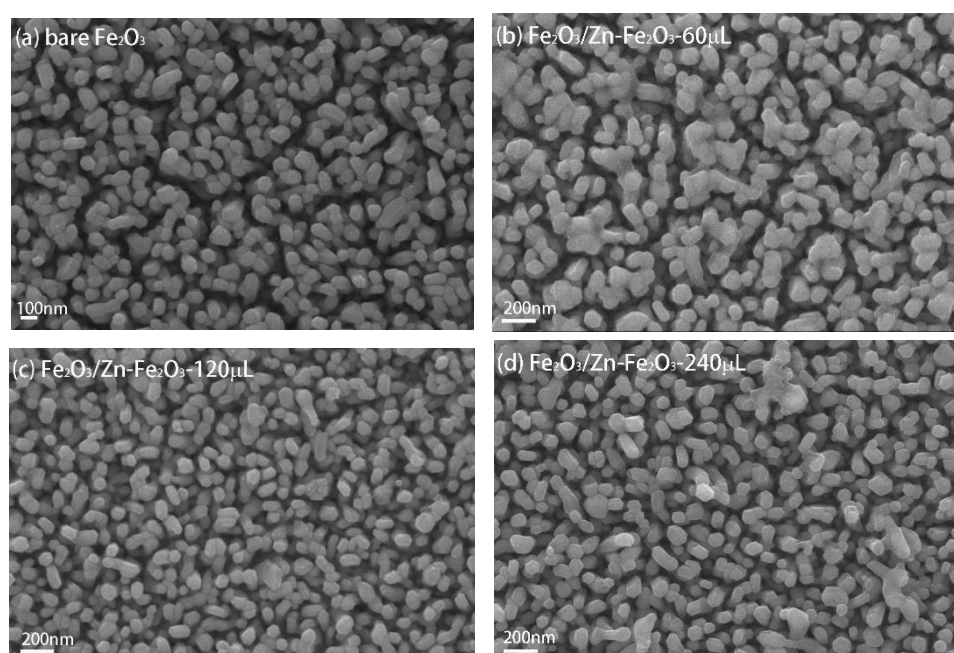


Figure 2. Scanning electron microscope images of the bare and surface-decorated hematite films

The microstructure and morphology of the bare and surface-modified hematite were examined by SEM, as shown in Fig. 2. The micrographs were taken from the top view of the hematite films. Hematite nanorods with diameters of approximately 70 nm grew separately and vertically to the FTO glass. After decoration with a thin layer of Zn-doped hematite, the nanorods partly coalesced. With the increasing amount of Zn-doped hematite, some irregularly shaped particles appeared on the surface of the hematite nanorods, which are aggregates of Zn-doped hematite particles.

X-ray diffraction was conducted for bare and modified samples, as shown in Fig. 3. Except for a set of peaks for SnO₂ (FTO), there are two additional prominent peaks located at 35.6° and 64.2°, which can be ascribed to the (110) and (300) facets of Fe₂O₃, respectively [18, 24]. No other chemical

phases were observed, indicating that Zn may have doped into the Fe_2O_3 catalyst or due to the low amount of the catalyst, which will be further verified by XPS later.

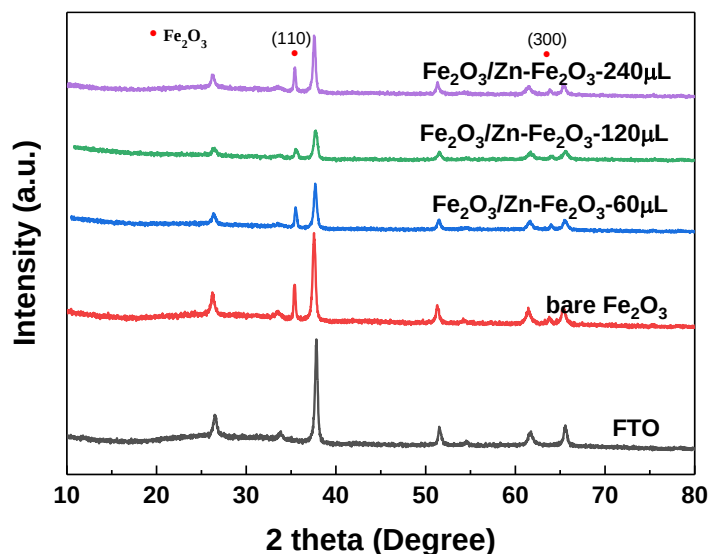


Figure 3. XRD pattern of bare and surface-modified Fe_2O_3 with different amounts of catalyst

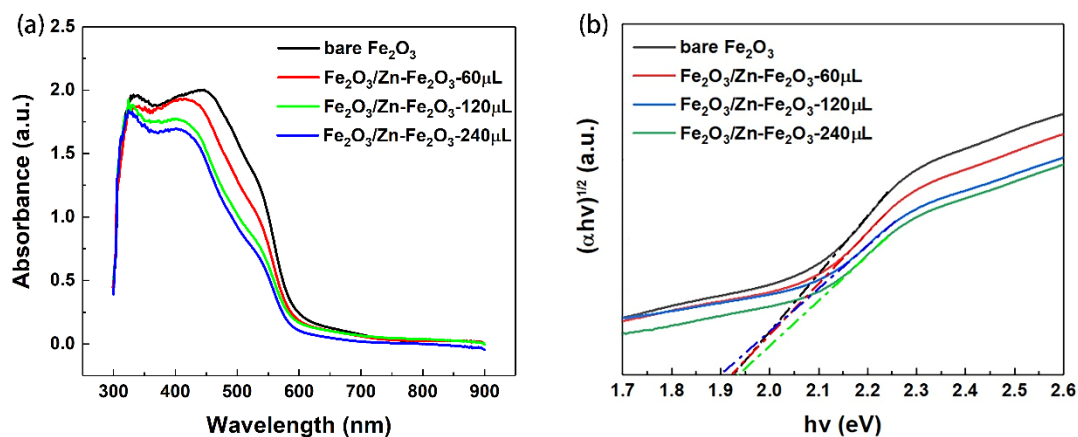


Figure 4. UV-Vis absorption spectra (a) and Tauc plots (b) of the bare and surface-decorated hematite films

To examine the changes in the optical properties, the UV-Vis spectra of the bare and modified samples were recorded. As shown in Fig. 4a, the absorbance decreased gradually with increasing amounts of OER catalyst, indicating that the amorphous catalyst layers slightly hindered light adsorption. The optical band gap energies were further determined by plotting the Tauc plots according to the following Tauc relationship [43]:

$$(\alpha h\nu)^n = A(h\nu - E_g) \quad (1)$$

where α is the absorption coefficient, $h\nu$ is the photon energy of i , E_g is the band gap energy, and the value of n depends on the nature of the transition. For Fe_2O_3 , as an indirect transition, n is taken as $1/2$ [44, 45]. Tauc plots were derived by plotting $(\alpha h\nu)^2$ as a function of $(h\nu)$. The band gap energies can be obtained by fitting the linear portion and extrapolating to the x-axis, where the intercept is the band gap energy. As shown in Fig. 3a (inset), the respective band gap energies ranged from 1.9-1.93 eV, which matches the reported band gap values for $\alpha\text{-Fe}_2\text{O}_3$ [7, 46, 47]. Surface-modified samples showed a larger band gap, in agreement with the blueshift of the UV-Vis spectra.

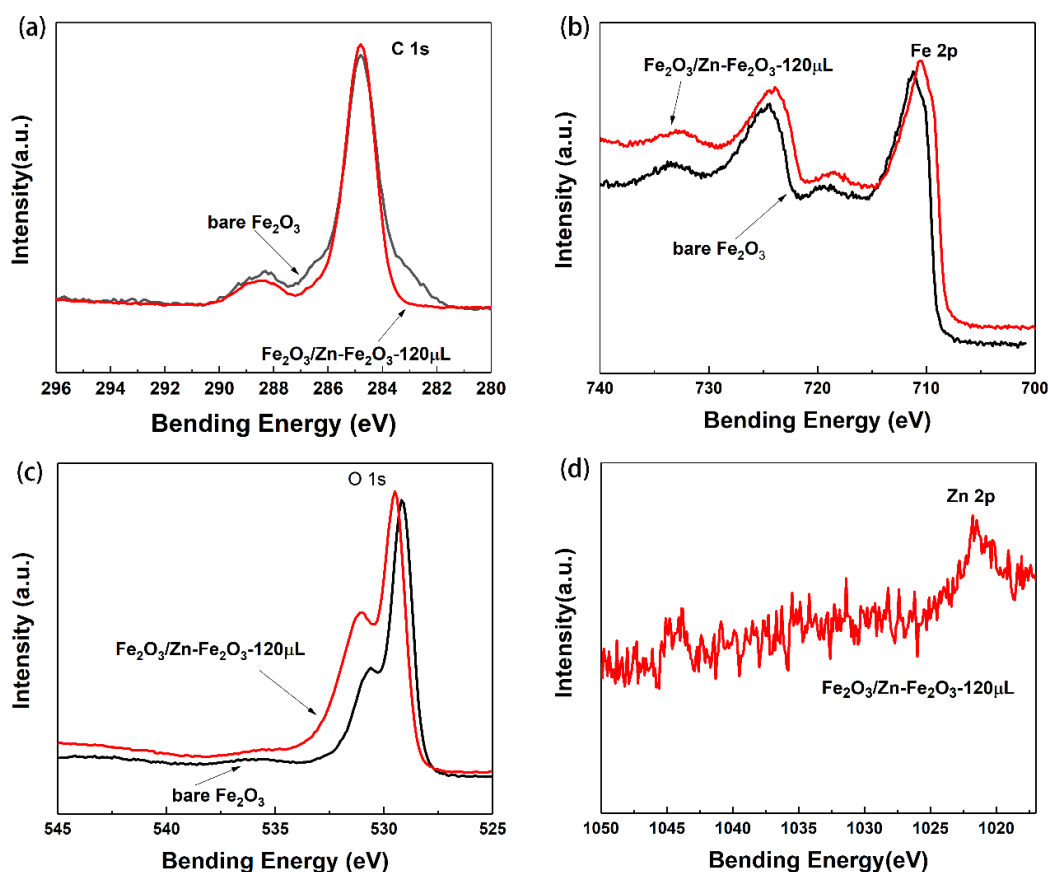


Figure 5. XPS spectra of bare hematite and surface-decorated hematite $\text{Fe}_2\text{O}_3/\text{Zn-Fe}_2\text{O}_3\text{-120 } \mu\text{L}$ films: a) C1s (b) Fe 2p (c) O 1s and (d) Zn 2p

The surface chemical composition and valence state of the bare and modified hematite $\text{Fe}_2\text{O}_3/\text{Zn-Fe}_2\text{O}_3\text{-120 } \mu\text{L}$ were analyzed with X-ray photoelectron spectroscopy (XPS). XPS spectra of the bare and modified samples are compared in Fig. 5, including C1s, O1s, Fe2p and Zn 2p. As shown in Fig. 5a, the peaks at 724.4 eV and 710.6 eV can be attributed to $\text{Fe } 2p_{1/2}$ and $\text{Fe } 2p_{3/2}$, respectively [46, 48, 49]. For sample $\text{Fe}_2\text{O}_3/\text{Zn-Fe}_2\text{O}_3\text{-120 } \mu\text{L}$, those peaks shifted to lower binding energies, implying coupling between core level electrons of Zn 2p with that of Fe 2p, suggesting a lower Fe valence state and the gain of electrons from Zn to Fe [49, 50]. This result is expected since

the electronegativity of Zn (1.6) is smaller than the electronegativity of Fe (1.8). The O1s XPS spectra in Fig. 5c exhibit a main peak located at 529.1 eV and a shoulder peak at 530. eV, which correspond to the Fe₂O₃ lattice and O-H or O-C bonds [51, 52]. In comparison to bare hematite, the main line and peaks for O1s of the surface-modified samples shifted to higher binding energies, indicating the effective introduction of Zn into the Fe₂O₃ lattice. As shown in Fig. 5d, the two peaks located at 1020 and 1044 eV can be ascribed to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively, confirming the presence of Zn²⁺ [48, 49, 53].

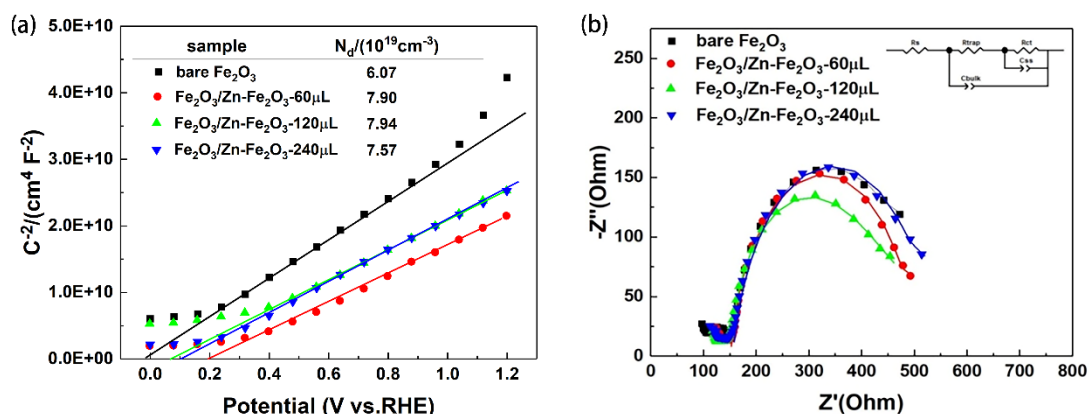


Figure 6. Mott-Schottky plots (a) and Nyquist plots (b) of the bare and surface-modified Fe₂O₃ with different amounts of catalyst

Table 1. Fitting results for EIS Nyquist plots

Samples	R _s	R _{trap}	R _{ct}	C _{ss}	C _{bulk}
Bare Fe ₂ O ₃	39.48	149.1	399	2.0195E-5	1.0989E-4
Fe ₂ O ₃ /Zn-Fe ₂ O ₃ -60 μL	1.4218E-6	142.7	353.9	1.7713E-5	4.2717E-5
Fe ₂ O ₃ /Zn-Fe ₂ O ₃ -120 μL	8.118E-6	112.5	342.2	3.2069E-5	5.3405E-5
Fe ₂ O ₃ /Zn-Fe ₂ O ₃ -240 μL	6.3847E-6	135.9	384.3	2.7697E-5	3.1457E-5

To check the electronic properties of the bare and surface-modified hematite, Mott-Schottky (M-S) measurements were conducted in 1.0 M NaOH in the dark at 1000 Hz, as shown in Fig. 6a. All the samples showed positive slopes, indicating that both bare and surface-modified α-Fe₂O₃ samples are n-type in nature, with electrons being the major charge carriers. The donor density (N_d) and the flat potential (V_{fb}) can be extracted by the M-S equation, as shown in Eq. (1):

$$\left(\frac{A_s}{C_{CS}}\right)^2 = \frac{2}{e\epsilon\epsilon_0 N_D} \left(V - E_{fb} - \frac{kT}{e}\right) \quad \text{Eq. (1)}$$

where A_s is the surface area of the electrode, C_{CS} is associated with the capacitance in the space charge region, e is the elementary charge, ε₀ is the permittivity of vacuum (8.854 × 10⁻¹⁴ C V⁻¹ cm⁻¹), ε is the dielectric constant of hematite (80 for hematite), V is the applied potential, k is Boltzmann's constant, E_{fb} is the flat-band potential and T is the absolute temperature. The results are listed in Fig.

6a. The donor density remains practically constant, in the range of $6.7\sim 7.9 \times 10^{19}$, in good agreement with the data of hematite in the literature [18, 24]. Actually, the deposition of a thin layer of catalysts would not influence the doping level [29]. However, the E_{fb} of the surface-modified samples exhibited a positive shift, which can be attributed to the change in the Helmholtz layer potential drop induced by the OER catalyst.

To elucidate the mechanism behind the photocurrent enhancement, electrochemical impedance was conducted in the dark and under illuminated conditions. As shown in Fig. 6b. Two semicircles can be observed, and the one at the high frequency (smaller one) region is associated with the electrochemical process in the bulk of the photoanodes, while the one at the low frequency (bigger one) region corresponds to the reaction process at the interface between the electrolyte and the photoanodes [38, 41, 54]. As shown in Fig. 6b, an equivalent circuit was used to fit the Nyquist plots of bare and surface-modified hematite. Herein, R_s refers to the series resistance in the system. R_{trap} corresponds to the charge trapping resistance from the conduction and valence bands to the surface state; C_{bulk} accounts for the capacitance of the space charge region in the bulk and Helmholtz layers; R_{ct} represents the charge transfer resistance from the surface of the photoanodes to the water; and C_{ss} accounts for the minority (hole) capacitance of the surface states existing on the surface of bare and modified hematite [55]. The R_{trap} , R_{ct} , C_{bulk} , and C_{ss} data are summarized in Table 1. The charge transfer resistance R_{ct} of the surface-modified samples is smaller than the charge transfer resistance of bare hematite, indicating that the decoration of the Zn-doped hematite catalyst facilitated charge transfer at the interface. The surface capacitance C_{ss} for the modified samples also increased slightly, indicating that more charges could be stored on the Zn-doped hematite surfaces. A correlation between the decrease in R_{ct} and increase in C_{ss} exists, indicating that hole transfer for OER takes place through the surface state, as reported in the literature [10, 11]. Compared with bare hematite, the R_{trap} for surface-modified samples also decreases. Since R_{trap} represents charge trapping resistance, the reduction in R_{trap} values indicates that the deposition of Zn-doped hematite also decreases the electron-hole recombination in the surface state, thereby facilitating the charge trapping efficiency.

In general, the PEC performance of photoelectrodes depends on three factors: light absorption, charge separation efficiency in the bulk ($\eta_{charge\ separation}$) and charge injection efficiency ($\eta_{charge\ injection}$) at the interface of hematite and electrolyte. Therefore, the photocurrent density collected in 1 M NaOH (J_{H_2O}) can be expressed by the following equation [56]:

$$J_{H_2O} = J_{absorbed} \times \eta_{charge\ separation} \times \eta_{charge\ injection} \quad \text{Eq. (2)}$$

where $J_{absorbed}$ is the theoretical photocurrent derived from the UV-Vis absorption spectra. $\eta_{charge\ separation}$ refers to the charge separation efficiency in the bulk, and $\eta_{charge\ injection}$ stands for the charge injection efficiency at the interface of the hematite and electrolyte. In a special case, when a strong hole scavenger, such as H_2O_2 [56, 57], is present in the electrolyte, the charge transfer from the hematite to H_2O_2 is very fast, so $\eta_{charge\ injection}$ is assumed to be 1 [18, 58, 59]. The $\eta_{charge\ separation}$ was directly determined. Then, $\eta_{charge\ injection}$ can be calculated with the $\eta_{charge\ separation}$ values. The $\eta_{charge\ separation}$ and $\eta_{charge\ injection}$ values versus applied potentials are plotted in Fig. 7a and 7b, respectively. In

comparison with bare hematite, the $\eta_{\text{charge separation}}$ for the modified samples slightly increased. For the $\eta_{\text{charge injection}}$, considerable enhancement was observed for the modified sample with more catalyst. The $\eta_{\text{charge injection}}$ reached 90% @1.23 V_{RHE} and 100% @1.4 V_{RHE}, indicating the excellent catalytic activity of the Zn-doped hematite layers.

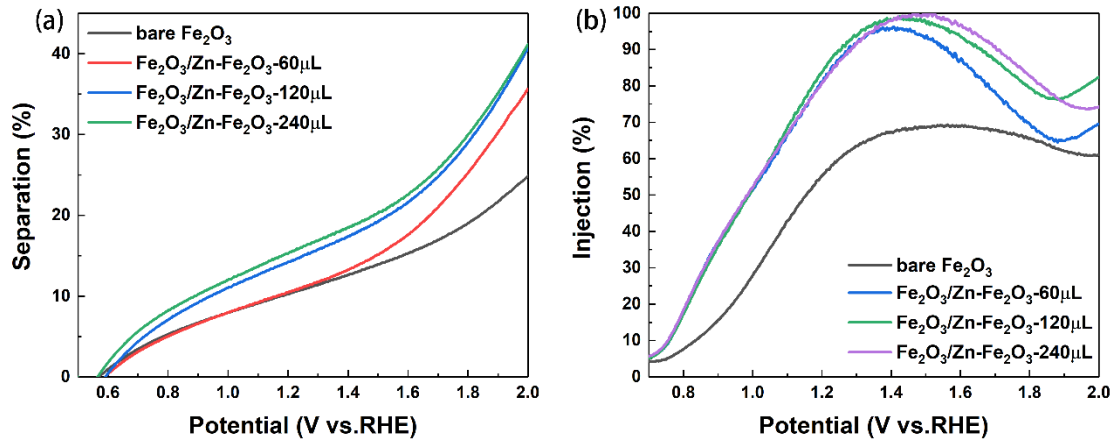


Figure 7. Charge separation (a) and injection efficiency (b) of bare and surface-decorated hematite films

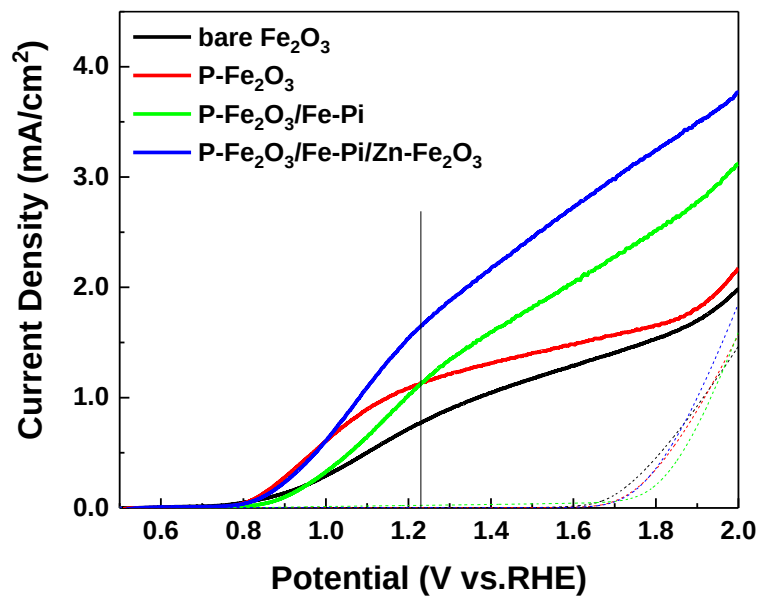


Figure 8. J-V characteristic curves of the bare and P-doped hematite films recorded in 1.0 M NaOH under illuminated (solid lines) and dark (dashed line) conditions

To study whether there is a synergistic contribution between different strategies, such as bulk doping, surface state passivation and surface catalysis, three different samples were prepared: (a) phosphorus-doped hematite, referred to as p-Fe₂O₃, (2) further surface passivated with amorphous FePO₄ layers, referred to as p-Fe₂O₃/Fe-Pi, and (3) further surface decorated with Zn-doped hematite catalyst, referred to as p-Fe₂O₃/Fe-Pi/Zn-Fe₂O₃. The J-V characteristic curves of these samples were

recorded in 1 M NaOH in the dark under illumination conditions. As shown in Fig. 8, the P-doped hematite increased the photocurrent over almost the whole potential window. However, there is an apparent saturated plateau in the potential window of 1.2 to 1.8 V_{RHE}, attributed to the Fermi level pinning effect induced by the surface state [60]. After passivation with amorphous FePO₄ layers, the photocurrent of sample p-Fe₂O₃/Fe-Pi increased more rapidly and without a significant saturated plateau in the measured potential window.

Table 1. Summary of PEC performance of Fe₂O₃-based photocathodes for water oxidation

Samples	Photocurrent density (mA/cm ²) at 1.23 V _{RHE}	Onset Potential (V _{RHE})	Reference
FTO/Fe ₂ O ₃ /Co ₃ O ₄	1.2	0.66	[32]
FTO/Fe ₂ O ₃ /Mg-Fe ₂ O ₃	0.5	0.8	[61]
FTO/Fe ₂ O ₃ /p-CaFe ₂ O ₄	1.06	0.88	[62]
FTO/TiO ₂ /Fe ₂ O ₃	1.1	1.06	[63]
FTO/Fe ₂ O ₃ /NiOOH	0.62	0.63	[29]
FTO/Fe ₂ O ₃ /FeOOH	1.21	0.65	[31]
FTO/Fe ₂ O ₃ /TiO ₂	1.3	0.9	[64]
FTO/Fe ₂ O ₃ /LaFeO ₃ /CoOx	1.12	0.95	[65]
FTO/S:Fe ₂ O ₃	1.42	0.82	[66]
FTO/P:Fe ₂ O ₃ /MnO ₂	1.65	0.9	[67]
FTO/Fe ₂ O ₃ /Co-MOF	2.0	0.6	[68]
FTO/Fe ₂ O ₃ /Fe ₃ O ₄	2	0.84	[69]
FTO/Fe ₂ O ₃ /CuO	0.7	0.87	[70]
FTO/W-Fe ₂ O ₃ /MoS ₂	1.87	0.64	[71]
FTO/Sn-Ti-Fe ₂ O ₃ /ZIF-67	2	0.9	[72]
FTO/Fe ₂ O ₃ /Fe(II) lactate	1.5	0.6	[73]
FTO/Fe ₂ O ₃ /Zn-Fe ₂ O ₃	1.34	0.7	This work
FTO/p-Fe ₂ O ₃ /Fe-Pi/Zn-Fe ₂ O ₃	1.65	0.7	This work

After further modification with the Zn-doped hematite catalyst, the photocurrent further increased to 1.65 mA and 2.0 mA at 1.23 and 1.4 V_{RHE}, respectively, indicating the presence of an excellent synergistic effect between the surface catalysis and other strategies. In addition, Table 1 presents a comparison of α -Fe₂O₃-based photoanodes decorated with different catalysts. Compared with other metal oxides, such as Mg-Fe₂O₃, p-CaFe₂O₄, CuO, and LaFeO₃, modification with the Zn-Fe₂O₃ catalyst in a simple spin-coating method can lead to a higher overall photocurrent density and a more negative onset potential. Normally, a reasonable combination of multiple strategies could lead to a higher photocurrent, such as FTO/Sn-Ti-Fe₂O₃/ZIF-67. Zn-doped hematite catalyst layers exhibited a synergistic effect with Fe-Pi passivation layers and were expected to be used in other complex photoanode systems.

4. CONCLUSIONS

Herein, a novel Fe-based OER catalyst, namely, Zn-doped Fe₂O₃, was deposited on the surface of hematite by a facile spin-coating method. Compared with bare hematite, all the surface-modified samples negatively shifted the onset potential by approximately 100 mV, and the photocurrent increased rapidly in a linear dependence on the bias. The sample spin-coated with an intermediate amount (120 μ L) of catalyst outperformed with the highest photocurrent density of 1.34 mA/cm² @ 1.23 V_{RHE}. Electrochemical impedance, Mott-Schottky, and H₂O₂ analyses were conducted to elucidate the role of the Zn-doped Fe₂O₃ deposits. With increasing amounts of catalyst, the charge transfer resistance was found to decrease with increased surface capacitance, indicating that the deposited Zn-Fe₂O₃ facilitates charge transfer effectively. Furthermore, the charge injection efficiency of all the surface-modified samples reached 90% @1.23 V_{RHE} and almost 100% @1.4 V_{RHE}, indicating the excellent catalytic activity of the Zn-doped hematite layers. After incorporation with other tactics, such as P doping and surface passivation, the photocurrent further increased to 1.65 mA and @1.23 V_{RHE}, and 2.0 mVA @1.4 V_{RHE}, respectively, indicating the presence of an excellent synergistic effect between surface catalysis and other strategies.

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