

MoNiP-modified hematite photoanode for stable and efficient photoelectrochemical seawater splitting

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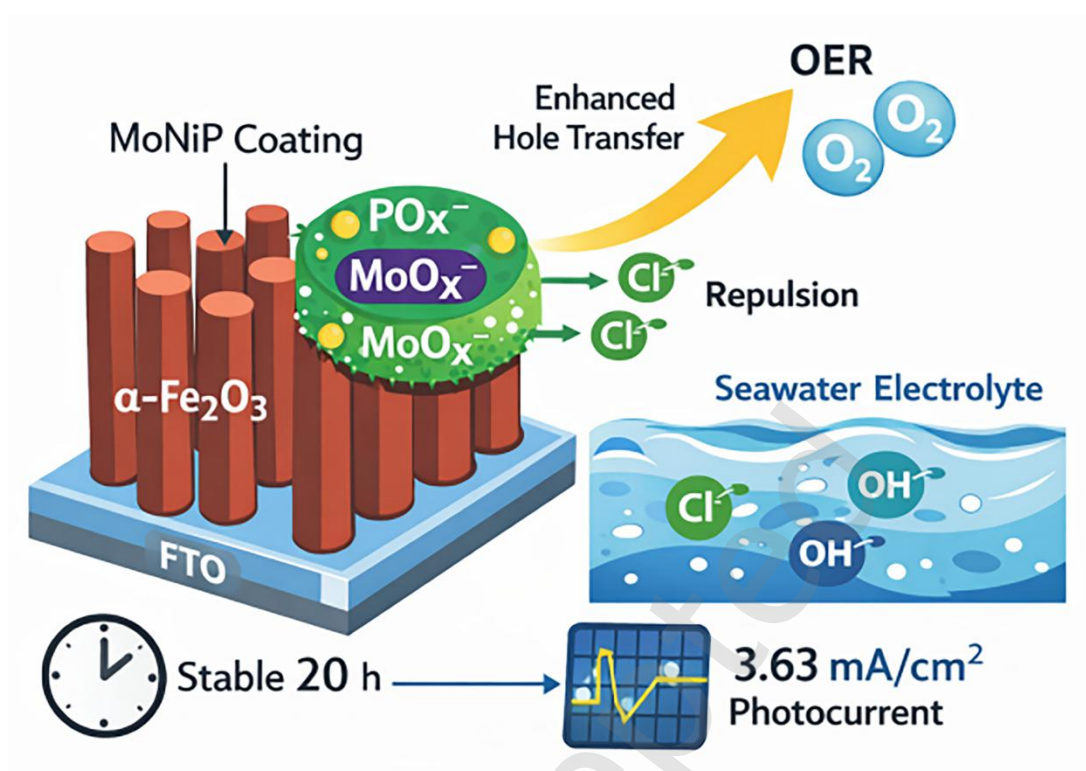
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MoNiP-coated Fe_2O_3 nanorod photoanodes enable chloride-tolerant photoelectrochemical seawater splitting. Surface $\text{PO}_x^{\delta-}$ and $\text{MoO}_x^{\delta-}$ species electrostatically repel Cl^- and accelerate hole transfer, delivering stable OER with a photocurrent of 3.63 mA/cm^2 over 20 h.

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ABSTRACT: Photoelectrochemical (PEC) seawater splitting is regarded as a promising route for sustainable hydrogen production. However, its practical application is limited by the sluggish oxygen evolution reaction (OER) kinetics and the corrosion of photoanodes induced by high chloride ion concentrations. Herein, we reported the construction of MoNiP layers on hematite (α -Fe₂O₃) photoanodes via a mild chemical deposition method, significantly enhancing both the stability and efficiency of seawater splitting. The incorporation of molybdenum modified the electronic structure of the photoanode, while PO_x^{δ-} and MoO_x^{δ-} surface species electrostatically repel chloride ions, effectively improving corrosion resistance. The optimized Fe₂O₃/MoNiP photoanode demonstrated a high photocurrent density of 3.63 mA/cm² at 1.23 V vs RHE. After 20 hours of continuous operation in simulated seawater, the photocurrent exhibited minimal decay. Moreover, the H₂ and O₂ evolution rates were in near-stoichiometric proportions, ensuring high OER selectivity. This study highlighted the synergistic effect of Mo and NiP in regulating interfacial charge dynamics and suppressing side reactions, providing new insights for the design of robust and efficient photoanodes for PEC seawater splitting applications.

KEYWORDS: Fe₂O₃/MoNiP photoanode, corrosion resistance, stability, photoelectrochemical seawater splitting

1 Introduction

PEC water splitting is widely regarded as a highly promising strategy for converting solar energy into hydrogen fuel with a zero carbon footprint [1-3]. Conventionally, water-splitting systems require ultrapure water as the feedstock to ensure optimal performance and long-term operational stability [4, 5]. In contrast to freshwater electrolysis, which relies on the limited availability of freshwater resources (<2.75% of the Earth's surface water), seawater electrolysis represents a more sustainable alternative, given that seawater constitutes approximately 96.5% of the planet's total water resources [6, 7]. Nevertheless, seawater splitting involves both the hydrogen evolution reaction (HER) and the oxygen evolution reaction (OER) [8, 9]. Among these, the OER occurring on the photoanode is particularly challenging due to its intrinsically sluggish reaction kinetics. Moreover, the high concentration of chloride ions (Cl⁻, ~0.5 M) present in seawater, which exhibit relatively low oxidation overpotentials, can induce competing side reactions such as the chlorine evolution reaction (CER) [10, 11]. These parasitic reactions result in the formation of hazardous chlorine species or hypochlorite, which can severely corrode photoanodes and compromise their stability [12, 13]. Therefore, the rational design and optimization of photoanode materials that can simultaneously achieve long-term stability and high

hydrogen production efficiency in seawater have become central objectives in current PEC research.

Among various photoanode materials, α -Fe₂O₃ has attracted considerable attention owing to its moderate bandgap (~2.1 eV), favorable valence band position, as well as its earth abundance and low cost [14-16]. In addition, KOH is commonly employed as the electrolyte for Fe₂O₃ photoanodes, where the high concentration of hydroxide ions (OH⁻) elevates the oxidation potential of Cl⁻, thereby effectively suppressing the CER and improving the performance of seawater splitting [17, 18]. Theoretically, α -Fe₂O₃ can deliver a maximum photocurrent density of approximately 12.6 mA/cm² under AM 1.5G illumination, corresponding to an upper solar-to-hydrogen (STH) conversion efficiency of ~15% [19, 20]. Despite these advantages, the practical performance of α -Fe₂O₃ photoanodes remains far below this theoretical limit [21, 22]. This discrepancy primarily arises from sluggish surface water oxidation kinetics and severe bulk and interfacial charge recombination [23, 24]. These intrinsic limitations underscore the critical need for advanced interface engineering and the rational design of catalytic and protective layers to enhance reaction selectivity, charge carrier utilization efficiency and corrosion resistance of Fe₂O₃ photoanodes in seawater splitting.

Transition metal phosphides (TMPs) have attracted increasing interest as effective surface functional layers for

photoanodes, owing to their high elemental abundance, excellent electrical conductivity and tunable electronic properties [25, 26]. These attributes make TMPs ideal for enhancing charge transfer at the interface and improving the kinetics of water oxidation reactions [27, 28]. For example, Feng et al. demonstrated the construction of ultrathin NiCoP nanosheets on Fe_2O_3 photoanode, which effectively improved charge carrier transport and enhanced the OER kinetics [29]. However, the fabrication of existing phosphide layers typically relies on high-temperature phosphidation processes under strict inert/reductive atmospheric conditions, often accompanied by the handling of toxic and corrosive phosphorus-containing byproducts [30]. Therefore, developing a simple, mild and scalable strategy for the construction and optimization of phosphide functional layers, to achieve efficient and stable seawater PEC water splitting, remains a persistent challenge.

Even with the incorporation of phosphide materials, achieving a synergistic combination of "high activity-high selectivity-long lifespan" for Fe_2O_3 photoanodes under seawater conditions remains a significant challenge. One of the core limitations is that Cl^- in seawater tends to adsorb/coordinate with transition metal active sites, occupying catalytic sites and inducing surface corrosion, thereby weakening the OER activity [31]. To mitigate the corrosion and side reactions induced by Cl^- , recent studies have proposed the use of negatively charged anions (such as MoO_4^{2-} , CO_3^{2-} , SO_4^{2-} , and F^-) to create an electrostatic repulsion environment on the electrode surface [32, 33]. This approach reduces the accumulation and attack of Cl^- at the interface, thereby enhancing the selectivity and stability of seawater oxidation. In particular, molybdenum-based species have garnered attention for their excellent corrosion resistance: for example, in the RuMoNi catalytic system constructed by Liu et al., in situ-generated MoO_4^{2-} during the reaction effectively repels Cl^- under seawater oxidation conditions, significantly suppressing chlorine-related side reactions and enhancing stability. Furthermore, molybdenum helps reduce the oxidation barrier of 3d metals (such as nickel) and facilitates the formation of higher oxidation states, thus enhancing OER activity. There is still a lack of feasible strategies for effectively introducing and stabilizing MoO_4^{2-} within phosphide-modified layers, simultaneously achieving chlorine corrosion resistance and controlling the phosphide active phase, thereby systematically improving the seawater PEC performance of Fe_2O_3 photoanodes.

Based on the aforementioned considerations, this study achieved the in situ loading of MoNiP layers onto Fe_2O_3 photoanodes through a mild (323 K) chemical deposition process. This strategy offered several advantages: I) The preparation of MoNiP/ Fe_2O_3 was accomplished through a simple, mild, and scalable approach; II) The electron configuration reconstruction induced by molybdenum enhanced the water splitting kinetics, while the PO_4^{3-} and MoO_4^{2-} anions effectively shield the electrode material from corrosion caused by Cl^- . The optimized photoanode delivered a photocurrent density of 3.63 mA/cm^2 and maintains stable performance for 20 hours under simulated seawater conditions.

2 Experimental

2.1. Materials

Fluorine-doped tin oxide (FTO) conductive glass ($1 \times 2 \text{ cm}$) was purchased from Advanced Election Technology Co., Ltd. All chemicals, including ferric chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$), sodium acetate (CH_3COONa), ethanol ($\text{C}_2\text{H}_6\text{O}$), Titanium Tetrachloride (TiCl_4), Nickel sulfate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), Sodium citrate pentahydrate ($\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$), Ammonium sulfate ($(\text{NH}_4)_2\text{SO}_4$), Sodium hypophosphite ($\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$), sodium molybdate (Na_2MoO_4), potassium hydroxide (KOH), and sodium sulfite (Na_2SO_3), were obtained from Sinopharm Chemical Reagent Co., Ltd., and used as received without further purification.

2.2. Preparation of Fe_2O_3 photoanodes

Fe_2O_3 photoanode was prepared on fluorine-doped tin oxide according to the previously reported method [34].

2.3. Preparation of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes

$\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes were prepared by depositing a Mo-doped NiP cocatalyst layer onto Fe_2O_3 electrodes through a mild electroless plating process at 323 K. The plating bath contained $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$ (2.50 g/100 mL) as the Ni source, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (1.50 g/100 mL) as the complexing agent, $(\text{NH}_4)_2\text{SO}_4$ (1.50 g/100 mL) as the buffer, $\text{NaH}_2\text{PO}_2 \cdot \text{H}_2\text{O}$ (3.00 g/100 mL) as the P source/reductant, and Na_2MoO_4 (0.20 g/100 mL) as the Mo source. The Fe_2O_3 photoanodes were immersed in 20 mL of preheated plating solution and kept at 323 K for electroless deposition. The plating solution was replaced at hourly intervals throughout the reaction process. After deposition, the samples were thoroughly rinsed with deionized water and stored in a vacuum-sealed container. A series of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes was obtained by varying the deposition time ($x = 15 \text{ min}$, 30 min , 1.0 h or 1.5 h). Moreover, the Mo/Ni feed ratio in the bath was tuned ($y/z = 0.05/1$, $0.10/1$, and $0.20/1$) to prepare $\text{Fe}_2\text{O}_3/\text{Mo}_y\text{Ni}_z\text{P}$ photoanodes. The sample prepared under the optimized deposition time and Mo/Ni feed ratio was denoted as $\text{Fe}_2\text{O}_3/\text{MoNiP}$. For comparison, a Mo-free control ($\text{Fe}_2\text{O}_3/\text{NiP}$) was synthesized under identical conditions without adding Na_2MoO_4 .

3 Results and discussion

3.1. Morphology and structure characterization

The schematic diagram shown in **Figure 1a** illustrated the growth process of MoNiP on Fe_2O_3 nanorods. First, Fe_2O_3 photoanodes were prepared via a hydrothermal method. Subsequently, the MoNiP layer was in situ formed through a chemical deposition process. X-ray diffraction (XRD) analysis did not observe any diffraction peaks corresponding to MoNiP, which was attributed to the low loading amount that falls below the detection limit of XRD (**Figure 1b**) [35].

The growth morphology of Fe_2O_3 was investigated using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). SEM analysis revealed that the Fe_2O_3 films exhibited a worm-like morphology (**Figure 1c**). However, after the deposition of NiP and MoNiP, a loading layer appeared on the surface of the Fe_2O_3 photoanode, confirming the successful loading of NiP and MoNiP (**Figure 1d** and **Figure 1e**). Additionally, TEM further confirmed the nanorod morphology of Fe_2O_3 (**Figure 1f**). High-resolution TEM (HR-TEM) analysis revealed distinct lattice fringes at

the interfaces, with varying interlayer spacings (**Figure 1g**). Fourier transform analysis confirmed that the interlayer spacings in **Figure 2g₁** and **Figure 2g₂** were 0.251 nm and 0.189 nm, corresponding to the (110) and (024) planes of Fe_2O_3 , respectively. Notably, an amorphous layer was observed on the surface of Fe_2O_3 , which further

corroborated the successful loading of MoNiP. Energy-dispersive X-ray (EDX) spectroscopy confirmed the presence of Fe, O, Ni, P, and Mo elements in the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films, validating that MoNiP was firmly adhered to the surface of Fe_2O_3 (**Figure 1h**).

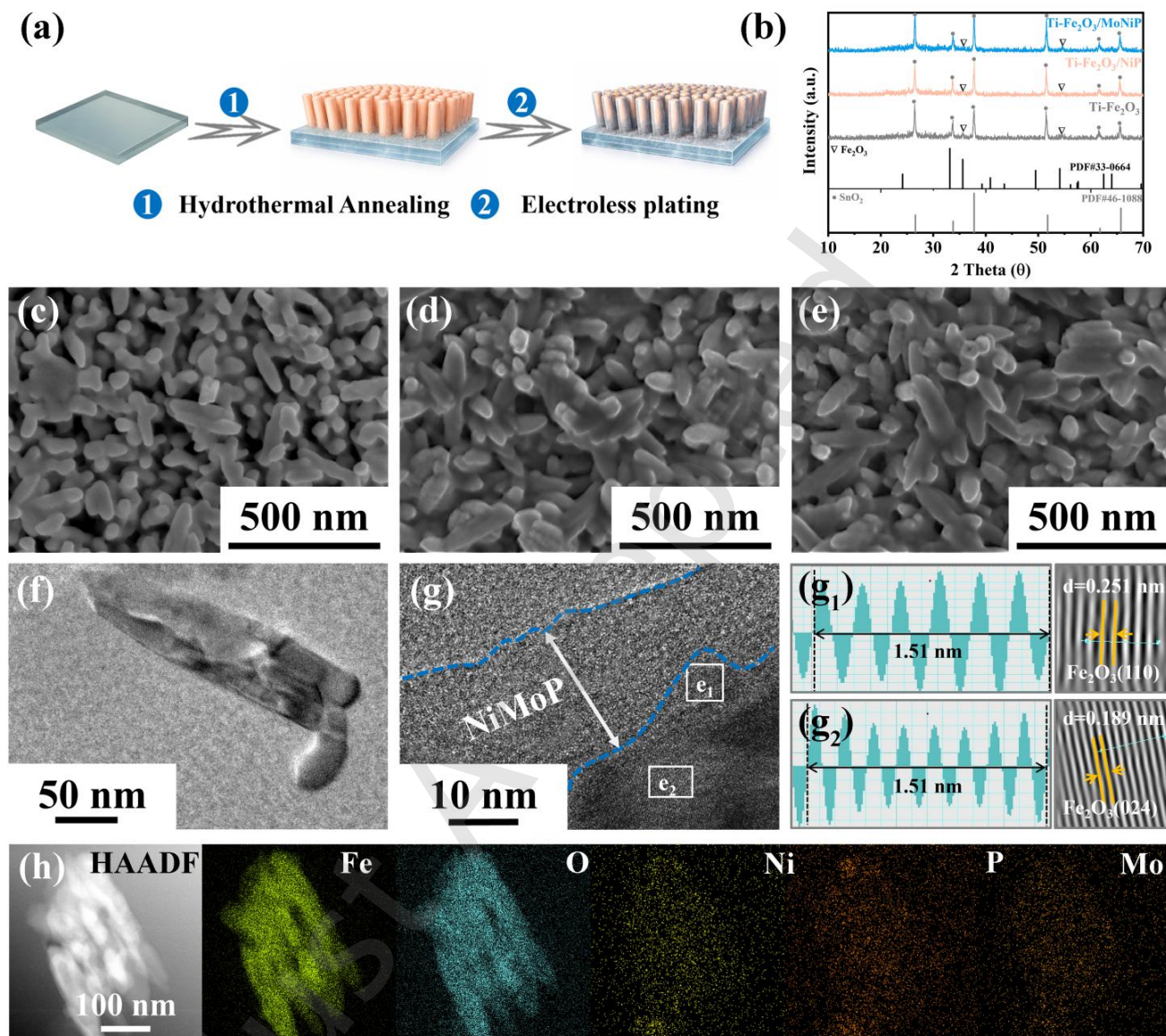


Figure 1. (a) Schematic diagram of preparing $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films. (b) XRD; SEM images of the (c) Fe_2O_3 , (d) $\text{Fe}_2\text{O}_3/\text{NiP}$ and (e) $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes. (f) TEM, (g) HRTEM and (h) EDX of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films.

X-ray photoelectron spectroscopy (XPS) was used to systematically examine the valence states and electronic structures of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films. The energy spectra of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ clearly revealed characteristic peaks corresponding to Ni, Mo, P, O, Fe and other elements (**Figure S1**). As shown in **Figure 2a**, the $\text{Fe } 2p$ XPS spectrum revealed three characteristic peaks, attributed to Fe^{2+} , Fe^{3+} and satellite peaks [36]. Compared to Fe_2O_3 , the $\text{Fe } 2p$ peaks of $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ exhibited slight negative shifts, indicating an increase in electron density at the Fe_2O_3 interface [37]. The $\text{O } 1s$ XPS spectra of all samples showed three distinct peaks, corresponding to adsorbed water (O_A), hydroxyl, oxygen vacancy (O_V) and lattice oxygen (O_L) (**Figure 2b**) [38]. The negative shift of the peaks after

surface modification further confirmed the strong interaction between Fe_2O_3 and the modified layer.

In the $\text{Ni } 2p$ spectra, the characteristic peaks of $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ were observed, both accompanied by satellite peaks for $\text{Ni } 2p_{3/2}$ and $\text{Ni } 2p_{1/2}$ (**Figure 2c**). The peak at 852.1 eV in the $\text{Ni } 2p$ spectrum of $\text{Fe}_2\text{O}_3/\text{NiP}$ and the peak at 851.5 eV in the $\text{Ni } 2p$ spectrum of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ can be attributed to Ni-P bonding. Compared to $\text{Fe}_2\text{O}_3/\text{NiP}$, the binding energy of surface oxidized nickel species in $\text{Fe}_2\text{O}_3/\text{MoNiP}$ showed a positive shift, and the peak area ratio ($\text{Ni}^{3+}:\text{Ni}^{2+}:\text{Ni}^0$) changed from 0.94:1.47:0.21 to 1.02:1.42:0.04. This indicated that the introduction of Mo reduces the electron density around the high-valent nickel species, thereby enhancing its chemical valence. In the $\text{P } 2p$ spectra of $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$,

characteristic peaks of metal P appear at approximately 129 eV and 130 eV, respectively. Additionally, the main peak at 133 eV in the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ spectrum and the peak at 132.8 eV in the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ spectrum corresponded to the P-O bonding signals of $\text{PO}_x^{\delta-}$ (**Figure 2d**). The presence of $\text{PO}_x^{\delta-}$ promotes the formation of metal oxidation states in the material, potentially increasing the number of catalytic active sites. Studies also suggested that these surface $\text{PO}_x^{\delta-}$ species can facilitate the reconstruction of surface active species during the OER. Regarding the introduced Mo component, the $\text{Mo } 3d$ spectrum showed two peaks at 232.1 eV and 235.3 eV, attributed to the high-valent Mo^{6+} species, indicating that molybdenum atoms predominantly exist in a higher oxidation state (**Figure 2e**). Furthermore, $\text{Ti } 2p$ peaks

in Fe_2O_3 was also observed, confirming the successful doping of Ti^{4+} (**Figure 2f**). The XPS studies revealed several key findings: 1) The local positive charge (δ^+) on nickel provided abundant adsorption sites for water and hydroxyl species, while the local negative charge (δ^-) on phosphorus facilitated efficient proton capture; 2) Molybdenum was generally in a high oxidation state, which may lead to the formation of $\text{MoO}_x^{\delta-}$ anions during water splitting, thereby preventing Cl^- from corroding the electrode; 3) The molybdenum component was successfully integrated into NiP, effectively modulating the electronic structure of the NiP catalyst and reducing the electron density around nickel atoms, thus optimizing the intermediate adsorption energies.

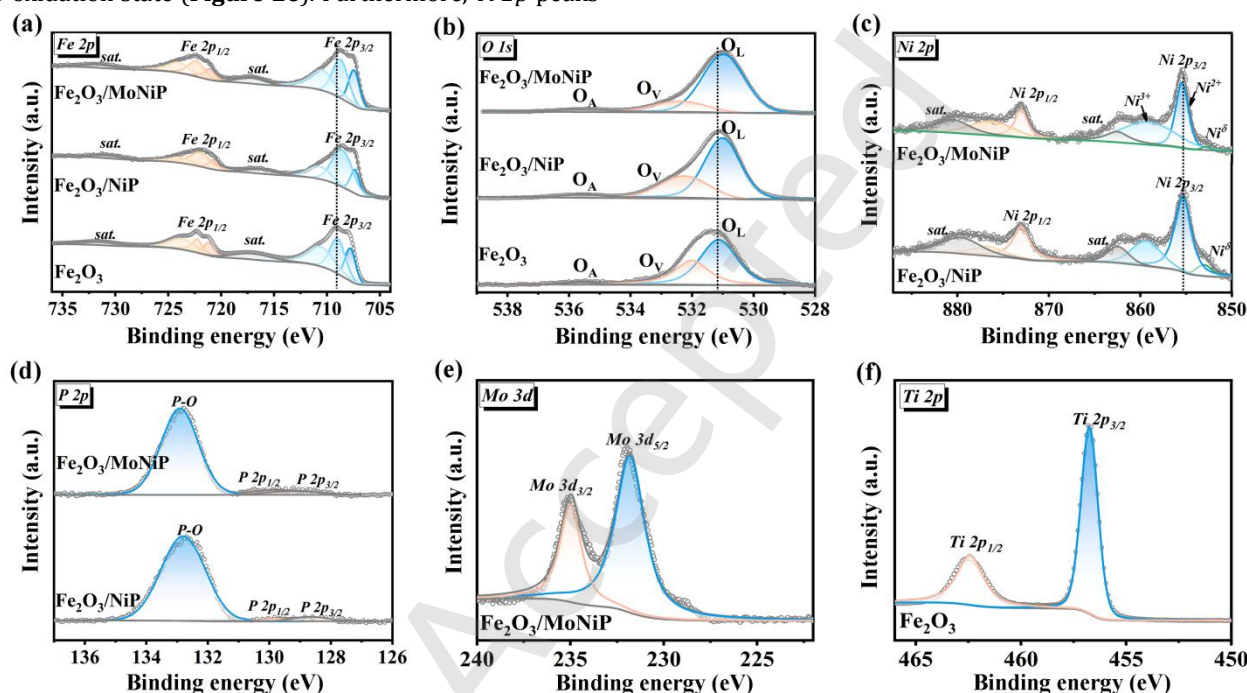


Figure 2. XPS spectra of (a) Fe 2p, (b) O 1s, (c) Ni 2p, (d) P 2p, (e) Mo 3d and (f) Ti 2p spectra from Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films.

3.2. PEC properties

To evaluate the PEC performance of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ in a simulated seawater electrolyte, PEC measurements were carried out in 1.0 M KOH + 0.5 M NaCl using a standard three-electrode configuration. All PEC tests were performed under AM 1.5G solar illumination provided by a xenon lamp with a light intensity of 100 mW/cm^2 . **Figure 3** compared the PEC performances of the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode and the corresponding control samples. As shown in **Figure 3a**, at 1.23 V vs. RHE, the pristine Fe_2O_3 photoanode delivered a photocurrent density of 0.82 mA/cm^2 in the chloride-containing alkaline medium. After introducing a phosphide cocatalyst layer onto the Fe_2O_3 surface, the photocurrent density was markedly enhanced under identical conditions. By further optimizing the deposition time and the Mo/Ni feeding ratio, the optimized $\text{Fe}_2\text{O}_3/\text{MoNiP}$ composite photoanode achieved a photocurrent density of 3.63 mA/cm^2 at 1.23 V vs. RHE, which was approximately three times that of Fe_2O_3 (**Figure S2**). In addition, the linear sweep voltammetry (LSV) results indicated that, compared with NiP, the incorporation of Mo further improves the PEC response of the composite photoanode, suggesting a more

effective promoting role of the MoNiP cocatalyst layer in this system. **Figure 3b** summarized the statistical distribution of performance metrics for Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$, evidencing stable sample-to-sample variations and good reproducibility.

Figure 3c showed the transient photocurrent responses of the photoanodes at 1.23 V vs. RHE. Fe_2O_3 exhibited a pronounced photocurrent decay during light on/off switching, which was commonly ascribed to intensified surface/interfacial charge recombination and sluggish surface reaction kinetics that lead to hole accumulation and subsequent recombination [39]. In contrast, the decay behavior was substantially mitigated for $\text{Fe}_2\text{O}_3/\text{NiP}$. Upon further incorporation of Mo, $\text{Fe}_2\text{O}_3/\text{MoNiP}$ displayed only a slight attenuation, indicating that the MoNiP cocatalyst layer can further suppress surface recombination and accelerate interfacial charge-transfer kinetics.

To quantitatively evaluate the charge-utilization capability, the performance enhancement of the Fe_2O_3 photoanode upon the introduction of MoNiP was further reflected in the applied bias photon-to-current efficiency (ABPE) and incident photon-to-current efficiency (IPCE)

results under an external bias (**Figure 3d** and **Figure 3e**). Comparative analysis of ABPE and IPCE revealed that $\text{Fe}_2\text{O}_3/\text{MoNiP}$ delivered consistently higher values than those of $\text{Fe}_2\text{O}_3/\text{NiP}$ and bare Fe_2O_3 , indicating that both NiP modification and Mo incorporation effectively promote the separation, transport, and utilization of photogenerated charge carriers.

In addition, the carrier density (N_d) was estimated from Mott-Schottky (M-S) measurements. As shown by the results, $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ exhibited markedly higher N_d values than pristine Fe_2O_3 , suggesting that surface

modification and the introduction of phosphide components contribute to an increased effective charge carrier density and improved charge transport properties (**Figure 3f**). When combined with the superior transient photoresponse and enhanced photoelectric conversion efficiency observed for the MoNiP system, these results reasonably suggested that Mo incorporation may further boost the PEC performance of Fe_2O_3 by modulating the electronic structure of Ni active sites, thereby optimizing interfacial charge transfer and reaction kinetics.

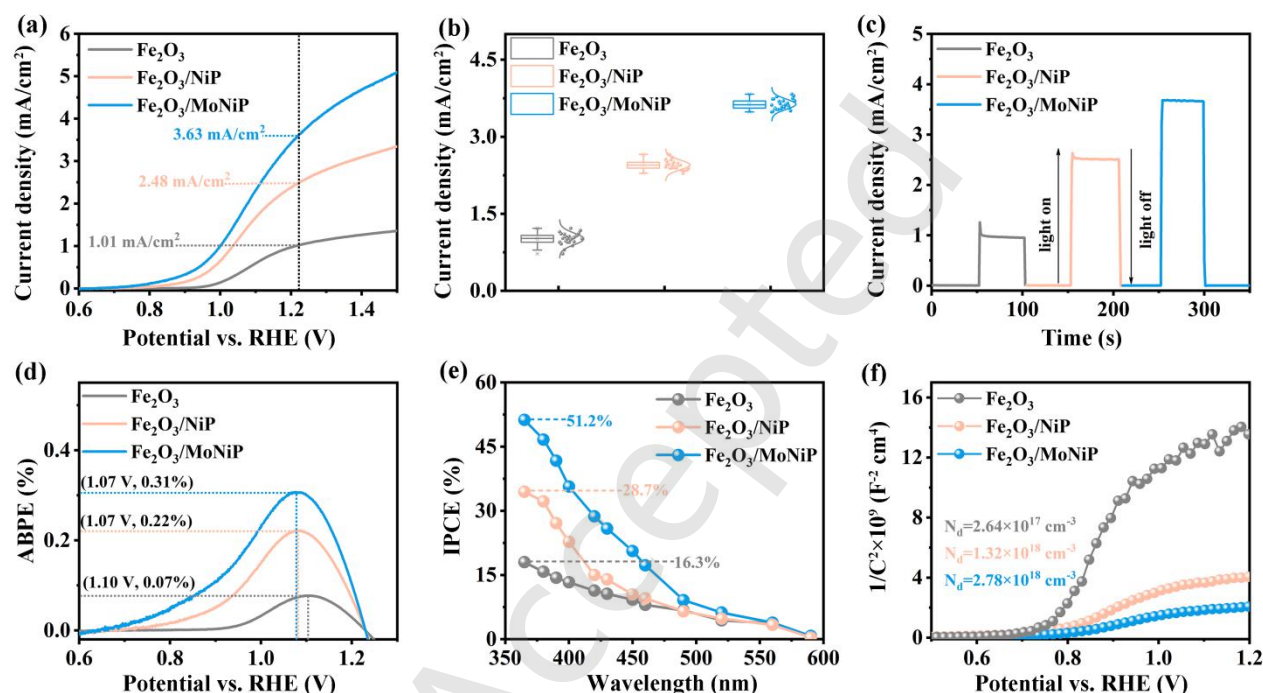


Figure 3. (a) LSV curves, (b) the statistical distribution of current density, (c) I-t, (d) ABPE, (e) IPCE and (f) M-S of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films.

3.3. PEC activity enhancement mechanism

The PEC performance of a photoanode is, in principle, positively correlated with the photon absorption rate (J_{abs}), the charge-separation efficiency (η_{sep}), and the charge-injection efficiency (η_{inj}) [40, 41]. To further elucidate the roles of the NiP and MoNiP modification layers and verify their contributions to the enhanced PEC activity, the optical and PEC properties of the modified photoanodes were systematically examined. UV-vis diffuse reflectance spectroscopy (**Figure 4a**) was employed to analyze the Fe_2O_3 photoanodes after NiP and MoNiP decoration. No discernible shift in the absorption edge was observed, indicating that variations in photon absorption were unlikely to be the dominant factor governing the PEC performance. To quantitatively assess η_{sep} and η_{inj} , measurements were conducted in an electrolyte containing Na_2SO_3 as a sacrificial hole scavenger. The results revealed that both NiP and MoNiP modifications markedly improved η_{sep} and η_{inj} (**Figure 4b** and **Figure 4c**), substantiating that the NiP and MoNiP layers played pivotal roles in facilitating charge separation and charge injection, in good agreement with the above analysis. The photoanode tested for η_{sep} and η_{inj} was subjected to XPS analysis, and no changes were observed compared to the original sample, confirming the

accuracy of the results ((**Figure S3**).

The charge-transfer characteristics of the Fe_2O_3 -based photoanodes, including the bulk resistance (R_{bulk}) and the photoanode/electrolyte interfacial charge-transfer resistance (R_{ct}), were evaluated by photoelectrochemical impedance spectroscopy (PEIS), as shown in **Figure 4d**. The inset illustrated the equivalent circuit model employed to fit the PEIS data. A pronounced reduction in R_{ct} indicated substantially improved interfacial charge-transfer kinetics, enabling more efficient transport of photogenerated charges to the electrode surface and thereby enhancing the overall PEC performance. Furthermore, to directly probe the influence of the catalyst overlayer on interfacial charge-transfer capability, Kelvin probe force microscopy (KPFM) was employed to map the surface potential distribution. As depicted in **Figure 4e**, both $\text{Fe}_2\text{O}_3/\text{MoNiP}$ and $\text{Fe}_2\text{O}_3/\text{NiP}$ photoanodes exhibited markedly higher surface potentials than pristine Fe_2O_3 under both illuminated and dark conditions, demonstrating that the NiP and MoNiP modification layers provide a stronger driving force for charge separation and extraction at the photoanode surface.

To monitor the charge-carrier dynamics in Fe_2O_3 -based photoanodes, photoluminescence (PL) spectroscopy was

employed. As shown in **Figure 4f**, the introduction of NiP and MoNiP modification layers led to a pronounced quenching of the PL emission intensity of Fe_2O_3 , highlighting their critical role in suppressing radiative recombination and promoting the separation and utilization of photogenerated charge carriers. Furthermore, carrier lifetimes were investigated by time-resolved photoluminescence (TRPL) measurements (**Figure 4g**). Both $\text{Fe}_2\text{O}_3/\text{MoNiP}$ and $\text{Fe}_2\text{O}_3/\text{NiP}$ photoanodes exhibited longer average carrier lifetimes (τ_{avg}) than that of Fe_2O_3 ($\tau_{\text{avg}} = 0.73$ ns), indicating that these modification layers enable more efficient utilization of photogenerated electrons and holes during the PEC process. This observation was in good agreement with the aforementioned analyses and further corroborated the beneficial role of NiP and MoNiP in regulating charge-carrier dynamics.

Based on the above results, the enhanced PEC performance of the photoanode can be primarily attributed to a synergistic effect arising from the reconstruction of interfacial charge processes and the acceleration of surface reaction kinetics. Upon the introduction of NiP, more efficient extraction and transport pathways for photogenerated holes were established, enabling their prompt participation in surface reactions and thereby mitigating surface/interfacial recombination induced by hole accumulation. Building on this effect, the further incorporation of Mo optimized the electronic structure and active sites of the modification layer, which in turn enhanced interfacial charge-transfer efficiency and facilitated more effective charge injection. Collectively, these improvements culminated in a substantially increased PEC performance.

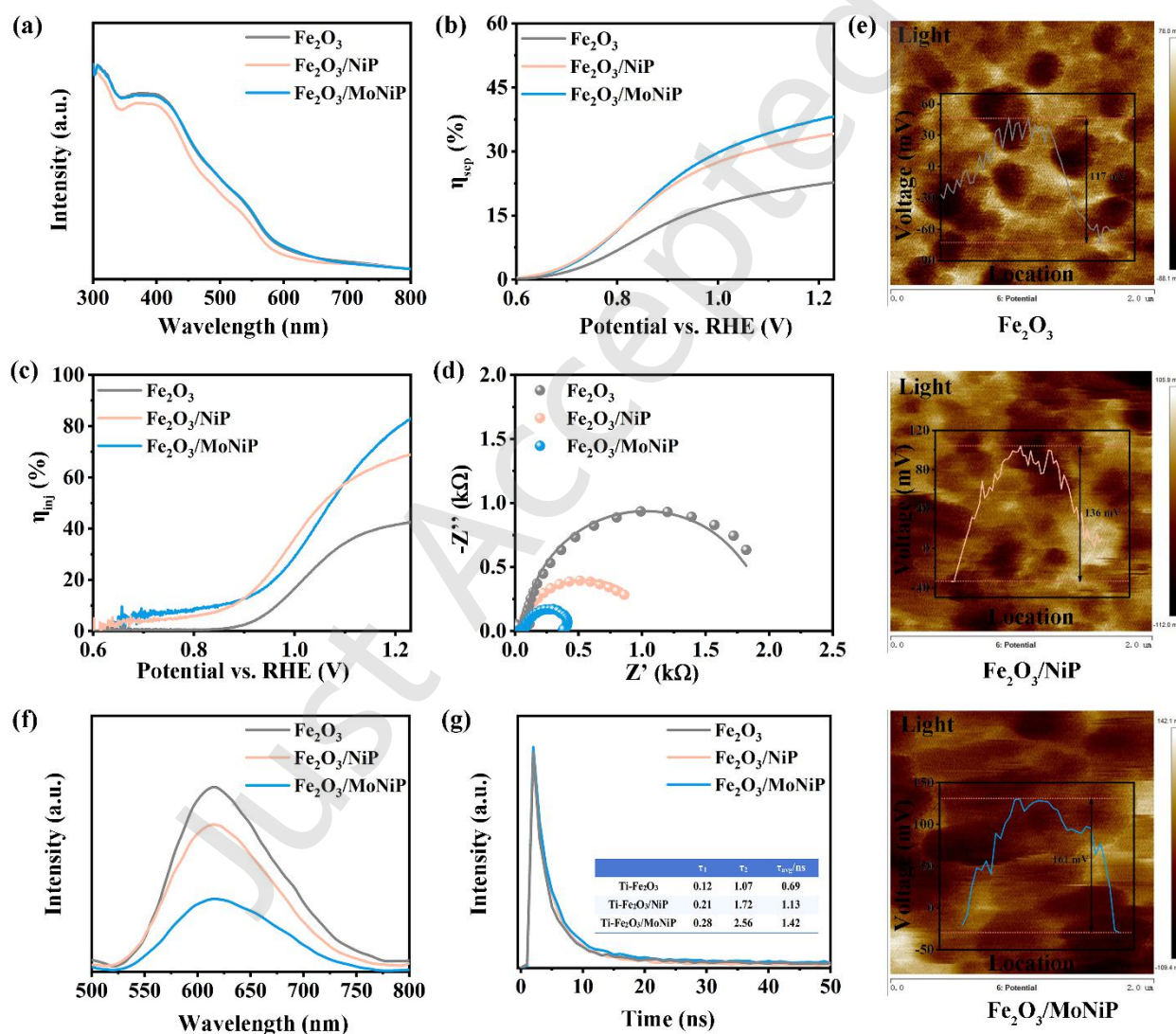


Figure 4. (a) UV-vis curves, (b) η_{sep} , (c) η_{inj} , (d) EIS, (e) KPFM, (f) PL and (g) TRPL of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ films.

To elucidate the impact of the overlayer on the OER kinetics of Fe_2O_3 photoanodes, systematic electrochemical characterizations were performed for different electrodes under dark conditions (**Figure 5a**). The LSV curves revealed a pronounced cathodic shift of the onset potential after introducing the catalytic layer, indicative of substantially facilitated OER kinetics. Further Tafel analysis (**Figure 5b**) shows that, compared with the Fe_2O_3 photoanode (330.9 mV

dec^{-1}), the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ electrode delivered a markedly reduced Tafel slope (109.3 mV dec^{-1}), suggesting accelerated reaction kinetics and faster interfacial charge-transfer processes. In addition, the electrochemically active surface area (ECSA) analysis (**Figure S5** and **Figure 5c**) demonstrated that the incorporation of NiP and MoNiP significantly increased the density of accessible active sites on the photoanode surface, thereby providing a more

favorable reaction interface for OER. Taken together, these results substantiated that NiP deposition effectively promoted the OER kinetics of Fe_2O_3 photoanodes. More importantly, the further incorporation of Mo synergistically enhanced the catalytic performance by modulating the electronic structure of the MoNiP layer, strengthening carriers transfer capability, and enlarging the ECSA, collectively leading to improved OER kinetics on Fe_2O_3 . However, considering the limited conductivity of Fe_2O_3 under dark conditions, these dark electrochemical results are discussed here as supportive evidence for the overall electrode behavior, rather than as a direct measurement of the intrinsic OER activity of the ultrathin overlayer itself.

Bode phase plots were employed to further analyze the effect of MoNiP layer (Figure 5d-f). At 0.7 V vs. RHE, pristine Fe_2O_3 exhibited a large phase angle in the low-frequency region, suggesting severe hole accumulation and sluggish oxygen evolution kinetics. After the introduction of NiP, the low-frequency phase angle decreased, suggesting improved hole extraction at the interface. $\text{Fe}_2\text{O}_3/\text{MoNiP}$ showed

significantly suppressed phase angles across the entire frequency range, demonstrating that Mo incorporation enhanced charge transport both in the bulk and at the interface. At 1.0 V, $\text{Fe}_2\text{O}_3/\text{MoNiP}$ demonstrated accelerated surface reaction kinetics and suppressed hole accumulation, whereas pristine Fe_2O_3 still suffers from evident kinetic limitations. At 1.3 V, $\text{Fe}_2\text{O}_3/\text{MoNiP}$ showed only a weak high-frequency response, reflecting enhanced bulk conductivity and minimized transport resistance [42]. Bode analysis confirmed that the synergistic coupling of Mo doping and NiP surface modification substantially improved charge transport and surface reaction kinetics, thereby boosting PEC performance.

Figure 5g showed the polarization curves of different photoanodes in seawater, further elucidating their corrosion resistance. The corrosion potential of pristine Fe_2O_3 was only -0.11 V vs RHE, indicating poor corrosion resistance (Figure 5h). After loading with NiP, the corrosion potential shifted positively to -0.08 V vs RHE, suggesting an improvement in corrosion resistance.

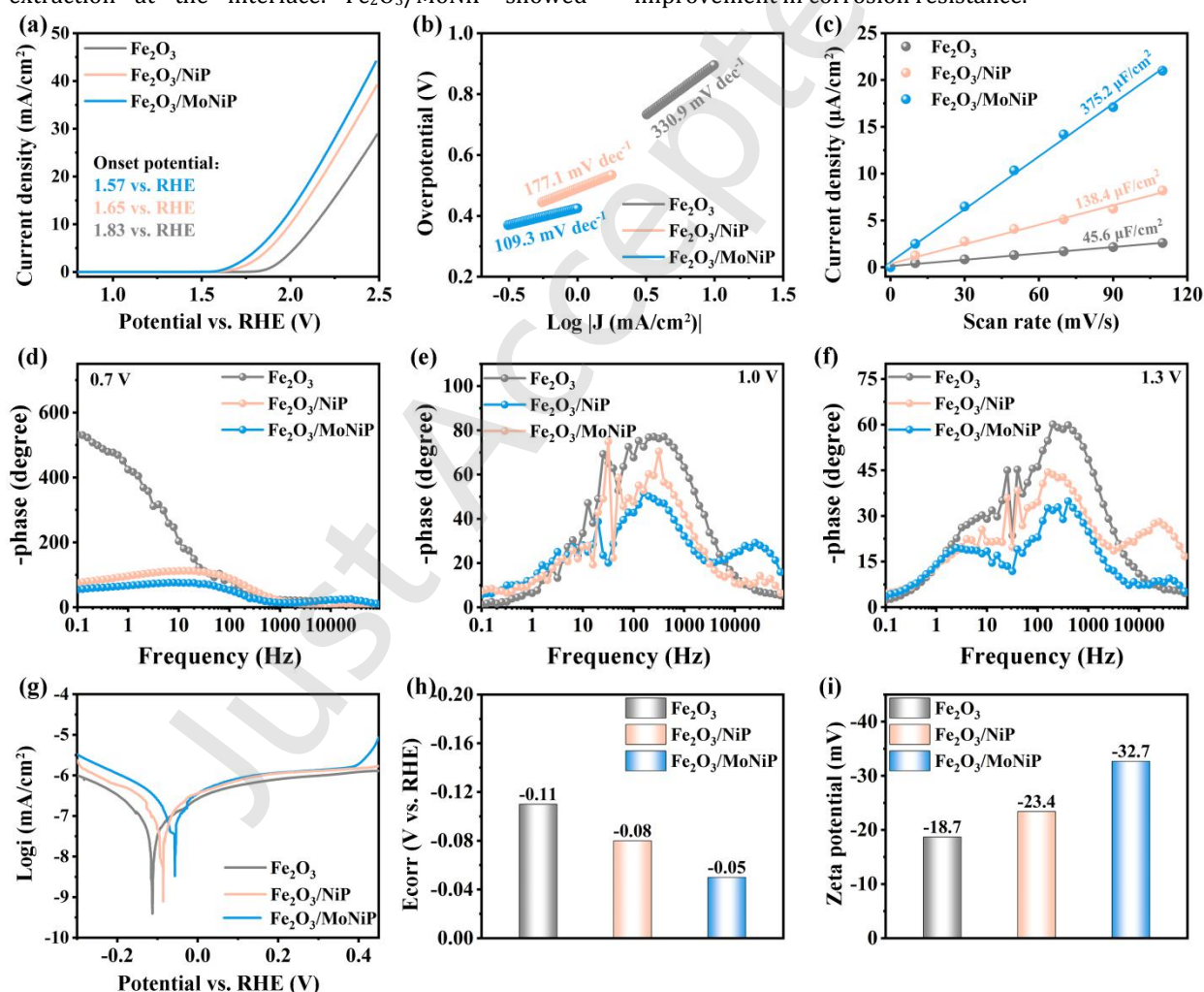


Figure 5. (a) LSV curves under dark, (b) Tafel, (c) ECSA, (d)-(f) Bode, (g) polarization curves, (h) corrosion potential and (i) zeta potential of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes.

Upon doping with Mo, the corrosion potential of Fe_2O_3 further shifts to -0.05 V vs RHE. Such improvement can be ascribed to the Mo incorporation, which induced the formation of an interfacial layer enriched with MoO_4^{2-} -related species on the photoanode surface, thereby

effectively suppressing Cl^- -induced attack. Zeta-potential measurements further corroborated this interpretation: compared with the undoped counterparts, the Mo-incorporated NiP overlayer exhibited the most negative zeta potential (-32.7 mV), strengthening the electrostatic

repulsion toward negatively charged Cl^- ions (**Figure 5i**). Consequently, the risk of chloride-triggered corrosion was mitigated, leading to improved operational stability of the photoanode in seawater environments.

3.4. PEC seawater splitting

During PEC seawater splitting, the H_2 and O_2 evolution behaviors of different photoanodes were summarized. Under continuous illumination for 2.5 h, the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode generated $192.69 \mu\text{mol cm}^{-2}$ of H_2 and $96.34 \mu\text{mol cm}^{-2}$ of O_2 , corresponding to an overall gas yield ~ 2.13 times higher than that of the bare Fe_2O_3 photoanode (**Figure 6a** and **Figure 6b**). Notably, the Fe_2O_3 photoanode exhibited an apparent deviation of the H_2/O_2 ratio from the theoretical 2:1 stoichiometry for water splitting. This discrepancy mainly originated from the seawater electrolysis environment, where a fraction of photogenerated holes was consumed by competing side reactions such as chloride oxidation, thereby suppressing the productive OER pathway. In contrast, the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode delivered a gas evolution ratio much closer to the theoretical value, indicating that MoNiP modification not only provided more efficient active sites for water oxidation but also effectively mitigated Cl^- -triggered side reactions and corrosion, thus improving both the selectivity and efficiency of overall water splitting. Moreover, cycling stability tests under illumination revealed no discernible decay in the H_2 and O_2 production rates of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ over four consecutive cycles (**Figure 6c**), underscoring its robust operational stability in seawater. Contact-angle measurements further showed that the

$\text{Fe}_2\text{O}_3/\text{MoNiP}$ surface is highly hydrophilic (**Figure 6d**), which facilitated electrolyte wetting and rapid bubble detachment, thereby further sustaining efficient PEC water splitting.

Stability is one of the key bottlenecks that hinders the practical implementation of PEC seawater splitting. To evaluate the operational durability of different photoanodes in seawater-like environments, long-term chronoamperometric tests were conducted under continuous illumination in a simulated seawater electrolyte (**Figure 6e**). The bare Fe_2O_3 photoanode exhibited rapid deactivation, with its photocurrent density decaying to 55% of the initial value after 5 h. In comparison, the $\text{Fe}_2\text{O}_3/\text{NiP}$ photoanode retained 90% of its initial photocurrent density after 10 h of uninterrupted operation, indicating that NiP modification partially improved the photoanode stability. Notably, the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode delivered a highly stable photocurrent output over 20 h with nearly negligible decay, demonstrating markedly enhanced long-term durability relative to the control electrodes. In addition, the morphology of the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode remained unchanged after the reaction (**Figure S6**). Post-reaction XPS analysis of the $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode revealed the disappearance of the Ni^{2+} signal and an increase in the Ni^{3+} peak intensity, indicating that part of the Ni species was oxidized during operation (**Figure S7**). Meanwhile, the O 1s spectrum exhibited an increased contribution from adsorbed oxygen (O_A), suggesting the partial transformation of MoNiP into oxyhydroxide species after reaction, which is consistent with the behavior commonly reported for metal phosphides under OER conditions [25]. The in situ formed

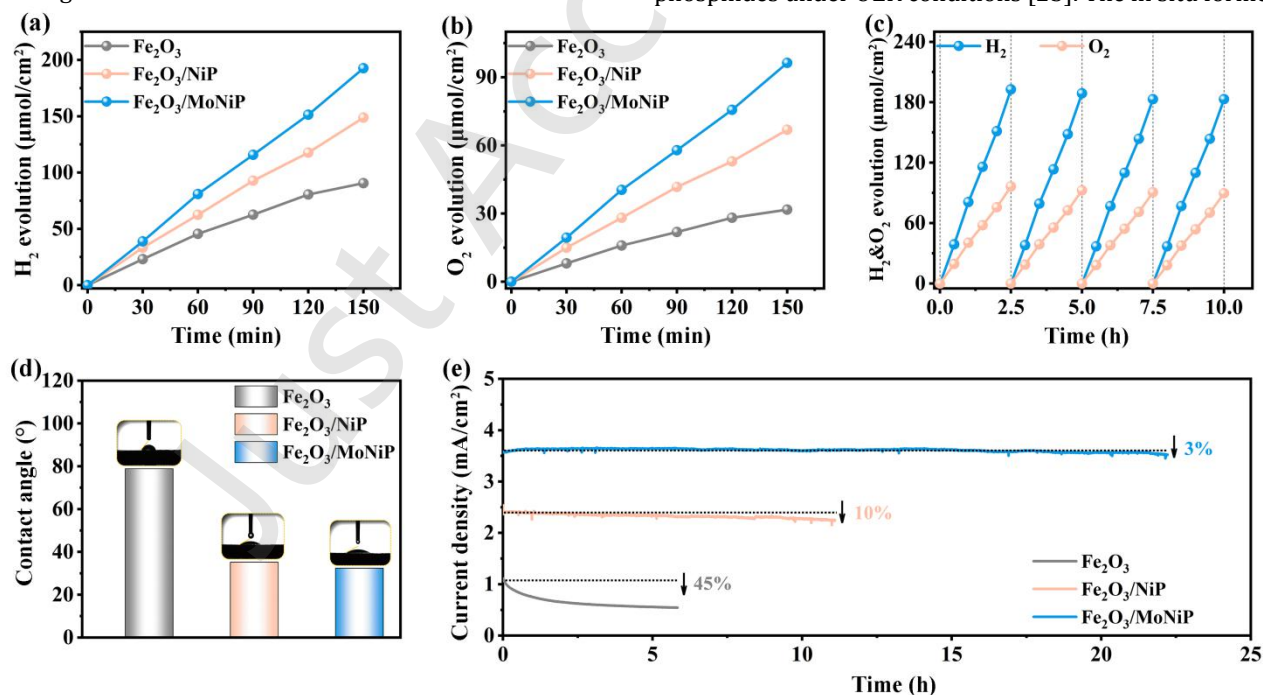


Figure 6. (a) H_2 and (b) O_2 evolution curves of samples of photoanodes; (c) recyclability measurement of $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode; (d) contact angle and (e) stability testing of Fe_2O_3 , $\text{Fe}_2\text{O}_3/\text{NiP}$ and $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes

oxyhydroxide layer can temporarily protect the photoanode surface and promote the oxygen evolution reaction; however, the corrosion induced by Cl^- remains severe. Importantly, the PO_4^{3-} and MoO_4^{2-} groups present on the MoNiP surface can repel Cl^- ions, thereby further suppressing chloride corrosion and enhancing the photoanode stability.

Collectively, these results verified that the MoNiP overlayer constructed on Fe_2O_3 via electroless deposition effectively strengthened the resistance against corrosion and deactivation in seawater, thereby enabling stable and efficient PEC seawater splitting.

4 Conclusions

In this study, we have developed a novel approach to enhance the performance and stability of Fe_2O_3 photoanodes for PEC seawater splitting by in situ depositing MoNiP layer through a mild chemical deposition method. The integration of Mo and NiP significantly improved the electronic structure and corrosion resistance of the photoanodes, addressing critical challenges such as slow OER kinetics and chloride-induced corrosion. The optimized $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanode exhibited a photocurrent density three times higher than the pristine Fe_2O_3 , along with excellent stability. Furthermore, the system demonstrated high OER selectivity with nearly stoichiometric H_2 and O_2 evolution, highlighting the effectiveness of the MoNiP cocatalyst in mitigating unwanted side reactions. The findings presented in this study pave the way for further advancements in PEC technologies, providing a solid foundation for the development of large-scale, sustainable hydrogen production from seawater.

Electronic Supplementary Material: Supplementary material (please provide the brief detail of the ESM) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94908850>.

Data availability

Additional data related to this paper may be requested from the corresponding author upon request.

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Declaration of competing interest

All the contributing author(s) report(s) no conflict of interests in this work.

Author contribution statement

Shanshan Jiang: Methodology, Data curation, Writing - original draft. **Dabo Liu:** Formal analysis. **Fangyu Ren:** Software. **Xiaoming Wang:** Supervision. **Songjie Wu:** Project administration. **Xiaoxing Fan:** Resources, Supervision, Writing-review & editing and Project administration.

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Electronic Supplementary Material

MoNiP-modified hematite photoanode for stable and efficient photoelectrochemical seawater splitting

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Experimental

2.1 Characterization equipment

Morphologies of Fe₂O₃-based thin films were characterized with a scanning electron microscope (SEM, Regulus 8100). X-ray Photoelectron Spectroscopy (XPS) testing was performed using a Thermo Scientific ESCALAB Xi+ Probe spectrometer with a monochromatic AlK α source (photon energy 1486.68 eV), a spot size of 400 μ m, pass energy of 100 eV, and energy step size of 1.0 eV to investigate elemental composition and chemical states. Optical properties of photoanodes were measured with a UH5700 Ultraviolet–visible spectroscopy (UV-Vis-NIR) model. The photoluminescence (PL) spectra were tested on F-7000 FL spectrophotometer under laser excitation of 320 nm. Time-resolved photoluminescence (TRPL) was examined by a second harmonic generated beam of a Ti:sapphire laser (800 nm wavelength, 100 fs pulse-width, and 82 MHz repetition rate). Static contact angles were measured with a contact angle meter, DONANOV5. Kelvin probe force microscopy (KPFM) measurements were performed using a MultiMode 8-HR system (Bruker, Germany). The gas evolution was analyzed by gas chromatography (GC1690, JieDao) with a three-electrode system at 1.23 V vs. RHE.

2.2 Photoelectrochemical measurements

A standard three-electrode system was used for measuring the PEC performance on an electrochemical workstation (Princeton Applied Research 2273) including Pt as a counter electrode, Ag/AgCl as a reference electrode, and Fe₂O₃-based photoanodes as working electrodes. The PEC performance was measured under 100 mW/cm² (AM 1.5G) on the back-side of photoanodes. Light irradiated into 1 cm² of photoanode which immersed in the 1 M KOH+0.5 M electrolyte. Electrochemical impedance spectroscopy (EIS) the frequency varied from 10 kHz to 0.1 Hz. Linear sweep voltammetry (LSV), EIS, and water splitting tests were all conducted under illumination. The remaining tests were conducted under dark conditions.

2.3 The equations

Eq. S1 was used to convert Ag/AgCl reference potential into RHE [1]:

$$V_{RHE} = V_{Ag/AgCl} + 0.197 + 0.059 \text{ pH} \quad \text{S1}$$

Where V_{RHE} is the potential vs. RHE, $V_{Ag/AgCl}$ is the potential vs. Ag/AgCl.

Eq. S2 was used to calculate N_d [2]:

$$\frac{1}{C^2} = \left(\frac{2}{e\epsilon\epsilon_0 N_d A^2} \right) \left(V - V_{fb} - \frac{k_B T}{q} \right) \quad \text{S2}$$

Where C was the space-charge capacitance, V (V vs. RHE) was the applied voltage, V_{fb} (V vs. RHE)

was the flat-band potential, N_d was the charge carrier density, ϵ was the dielectric constant of the semiconductor (40 for TiO_2). ϵ_0 was the vacuum permittivity ($8.854 \times 10^{-12} \text{ F/m}$), k_B was the Boltzmann constant ($1.38 \times 10^{-23} \text{ J K}^{-1}$), q was the electronic charge ($1.60 \times 10^{-19} \text{ C}$), and T was the absolute temperature (298K).

Eq. S3 was used to calculate η_{bulk} [3]:

$$\eta_{bulk} = \frac{J_{Na_2SO_3}}{J_{abs}} \quad \text{S3}$$

Where the $J_{Na_2SO_3}$ was the photocurrent density measured in 0.5M Na_2SO_4 and 0.5 M Na_2SO_3 mixed electrolyte, which served as hole scavengers to ensure the hole injection rate approaching 100%.

Eq. S4 was used to calculate **ABPE** [4]:

$$ABPE = \frac{J(1.23 - V_b)}{P} \times 100\% \quad \text{S4}$$

Eq. S5 was used to calculate **IPCE** [5]:

$$IPCE = \frac{J \times 1240}{\lambda \times P_{light}} \times 100\% \quad \text{S5}$$

Where J is the photocurrent density (mA/cm^2); λ is the incident light wavelength (nm); P_{light} is the power density (mW/cm^2).

Photoluminescence decay curves, and the average recombination lifetime, $\tau_{average}$ was calculated by the following Equation [6]:

$$R(t) = B_1 e^{-t/\tau_1} + B_2 e^{-t/\tau_2} \quad \text{S6}$$

$$\tau_{average} = \frac{B_1 \tau_1^2 + B_2 \tau_2^2}{B_1 \tau_1 + B_2 \tau_2}$$

S7

In the formula, and are defined as the decay time for the fluorescence intensity, τ_1 and τ_2 representing the speed of carrier recombination.

Eq S4 was used to calculate **The Faraday efficiencies** [7]:

$$H_2(\text{or } O_2) \mu\text{mol.cm}^{-2} = \left(\frac{\text{Area of } H_2(\text{or } O_2) \text{ peak}}{\text{Slope of calibration curve for } H_2(\text{or } O_2)} \right) \times (\text{Head space volume}) \times \left(\frac{1 \text{ mol}}{24.2 \text{ L}} \right)$$

S8

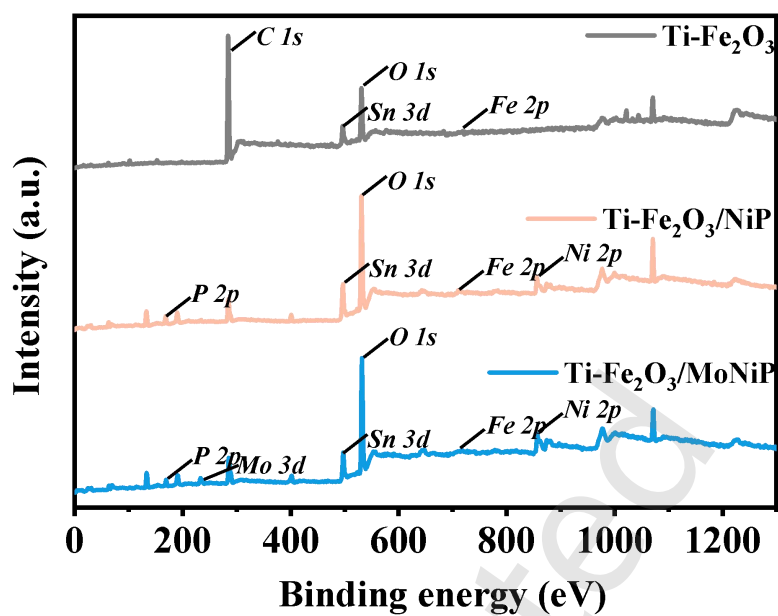


Figure S1 XPS spectrum of $\text{Ti-Fe}_2\text{O}_3$, $\text{Ti-Fe}_2\text{O}_3/\text{NiP}$ and $\text{Ti-Fe}_2\text{O}_3/\text{MoNiP}$ films.

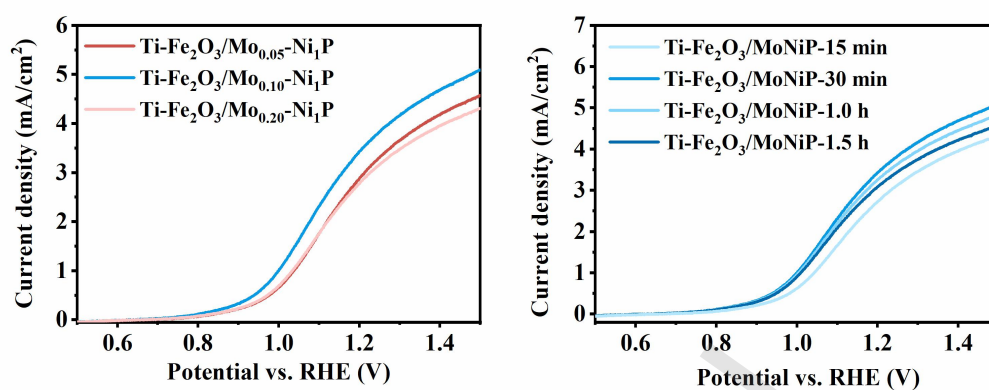


Figure S2. Optimization of preparation of Ti-Fe₂O₃/MoNiP photoanode.

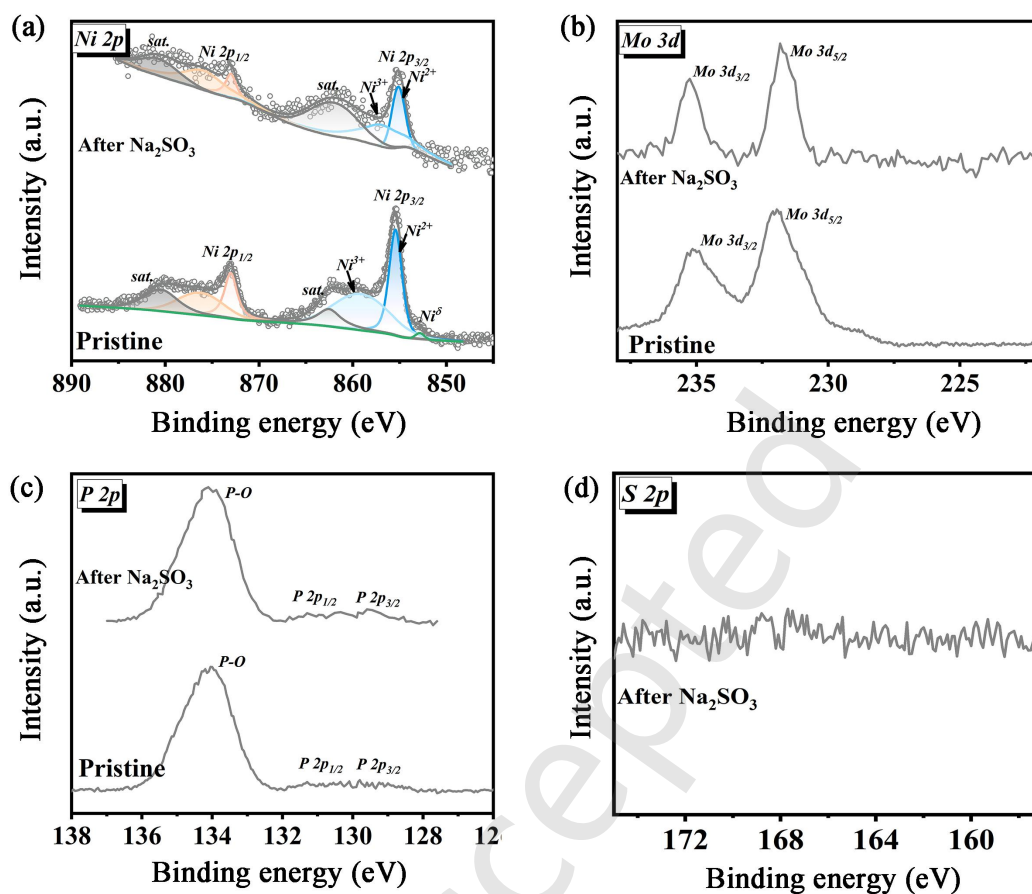


Figure S3. XPS of Fe₂O₃/MoNiP photoanodes after η_{sep} and η_{inj} test.

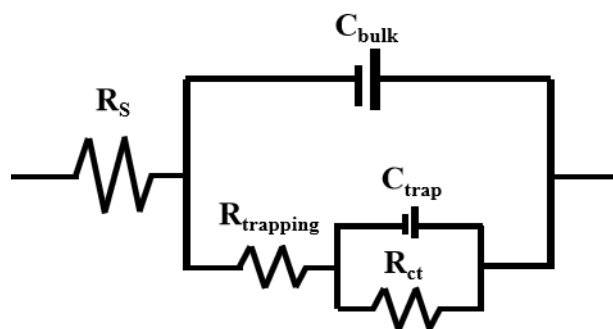


Figure S4. Nyquist plots fitted circuit model.

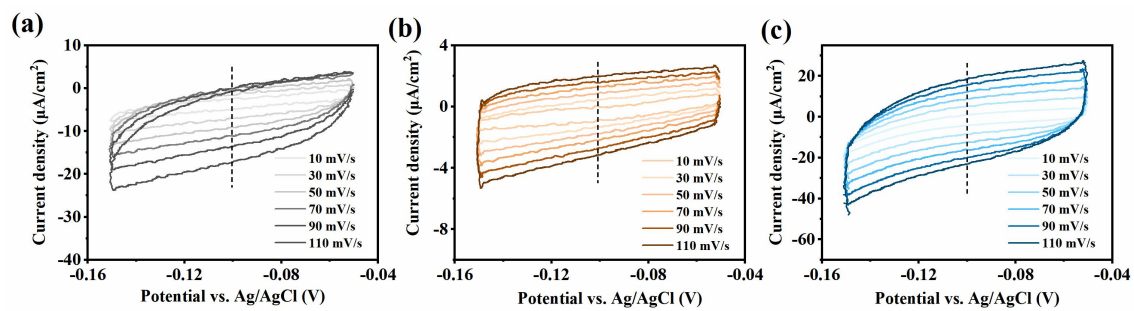


Figure S5. CV curves of (a) Fe_2O_3 , (b) $\text{Fe}_2\text{O}_3/\text{NiP}$, (c) $\text{Fe}_2\text{O}_3/\text{MoNiP}$ photoanodes.

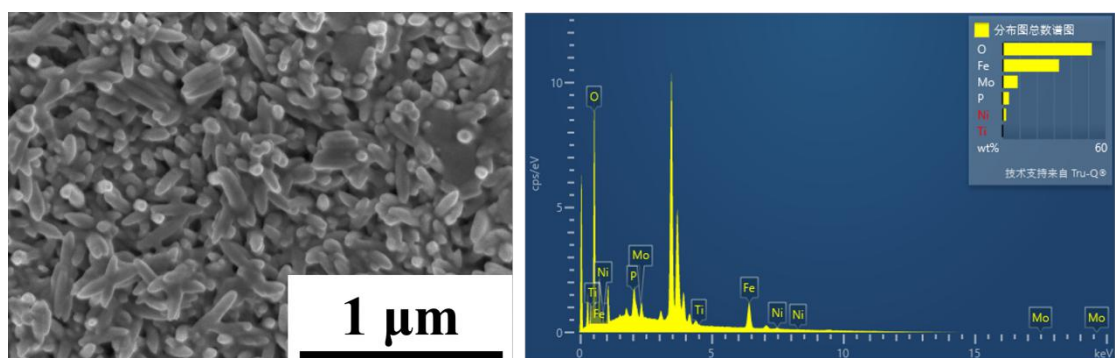


Figure S6. SEM images after long-term J-t test.

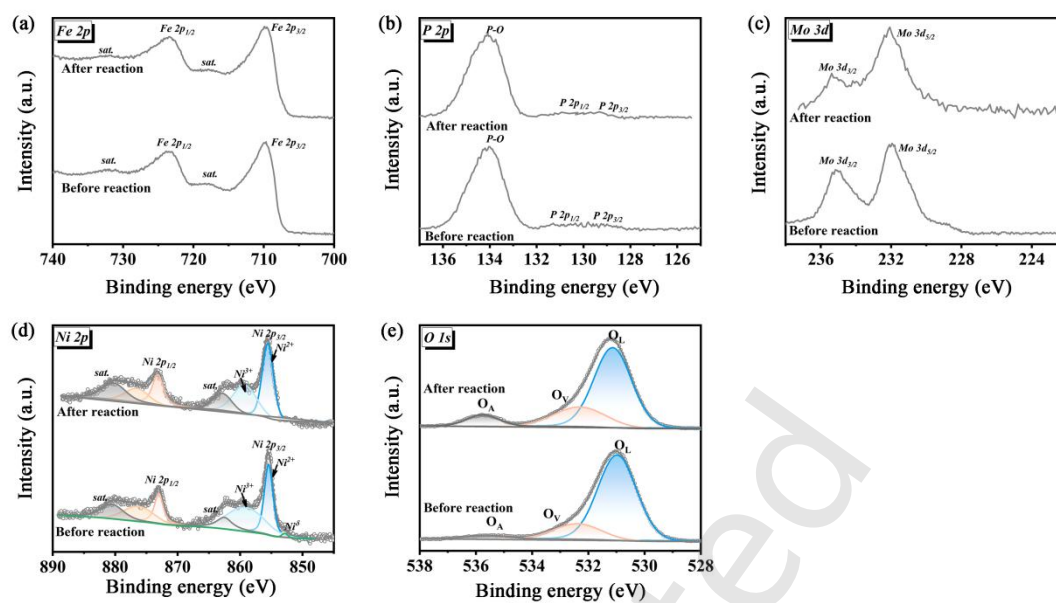


Figure S7. XPS of Fe₂O₃/MoNiP photoanodes after long-term J-t test.

Table S1 Photoelectrochemical Impedance Spectroscopy (PEIS) fitting parameters for Fe₂O₃, Fe₂O₃/NiP and Fe₂O₃/MoNiP films.

Samples	R_s (Ω)	R_1 (Ω)	R_2 (Ω)	C_{bulk} (μ F)	C_{ss} (μ F)
Fe ₂ O ₃	11.6	118.3	1938.4	27.4	268.2
Fe ₂ O ₃ /NiP	11.8	85.9	845.9	58.4	650.5
Fe ₂ O ₃ /MoNiP	12.3	69.0	394.2	152.6	2430.3

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