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Hybrid microwave annealing-induced formation of an α -Fe₂O₃/ZnWO₄ interface for photoelectrochemical water splitting and study of its charge transport mechanism

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The α -Fe₂O₃ photoanode is an efficient semiconductor material for photoelectrochemical (PEC) water oxidation due to its favorable bandgap, chemical stability, and natural abundance. However, the rapid recombination of photoexcited electrons (e⁻) and holes (h⁺) impedes the PEC efficiency. Herein, an α -Fe₂O₃/ZnWO₄ heterojunction photoanode was synthesized by combining hydrothermal and hybrid microwave annealing methods. The α -Fe₂O₃/ZnWO₄ heterojunction photoanode demonstrated a photocurrent density of 0.86 mA cm⁻² at 1.23 V vs. RHE, which is more than 2.2 times that of pure ZnWO₄ (0.06 mA cm⁻²) and the α -Fe₂O₃ photoanode (0.29 mA cm⁻²). In contrast, the α -Fe₂O₃/ZnWO₄ photoanode exhibited an improved ABPE value of 0.10% at 1.0 V vs. RHE. The significantly improved charge separation efficiency and reduced charge recombination were attributed to hole storage in a ZnWO₄ heterojunction layer.

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1. Introduction

There is an urgent need to develop clean and sustainable energy technologies due to the severe global environmental pollution caused by the excessive utilization of fossil fuels such as coal and petroleum energy resources.^{1,2} Hydrogen is a promising renewable energy source that would adequately supply energy for the entire planet.^{3,4} Researchers are interested in hydrogen energy (H₂) through water splitting using a photoelectrochemical (PEC) cell because it is a clean, zero-emission process that is environmentally friendly and low-cost, among many other alternatives and renewable energy sources.^{5,6}

In 1972, the TiO₂ semiconductor was first employed by Honda and Fujishima to split water through the PEC system.⁷ Additional semiconductor materials such as BiVO₄,⁸ TiO₂,⁹ ZnO,¹⁰ WO₃,¹¹ and α -Fe₂O₃ (ref. 12) have been investigated for PEC water oxidation. Among them, α -Fe₂O₃ is an especially promising semiconductor candidate for water oxidizing due to its excellent stability and environmental friendliness, low-cost, and suitable band gap ($E_g \approx 2.1$ eV). However, the more practical application of pure α -Fe₂O₃ is limited by several challenges, including low electron mobility, a short hole-diffusion length (2–4 nm), a low light absorption coefficient resulting

from its indirect band gap, and short carrier lifetime. Moreover, the conduction band edge position of a pure α -Fe₂O₃ photoanode does not align with the reversible hydrogen potential, necessitating a high over-potential for PEC water reduction. Further, the use of an α -Fe₂O₃ photoanode is more challenging for efficient water oxidation due to its low PEC water oxidation kinetics and inefficient charge separation.

Several approaches have been employed to address the challenges associated with using α -Fe₂O₃ for PEC water splitting, such as doping,¹³ nanostructuring photoanodes,¹⁴ and the formation of heterojunction photoanodes.¹⁵ During the water oxidation reaction, the charge separation of electrode surfaces is promoted by nanostructuring of the α -Fe₂O₃ photoanode. Various nanostructured forms of α -Fe₂O₃ have been reported with surface morphologies of nanorods,¹⁶ nanotubes,¹⁷ nanosheets,¹⁸ and nanoflowers.¹⁹ One effective method that has been widely used to reduce charge recombination, improve photon absorption, and improve charge separation of α -Fe₂O₃ for effective PEC water splitting is the development of heterojunction structures.

For example, Alotaibi *et al.* reported an α -Fe₂O₃/TiO₂ heterojunction photoanode created by a chemical vapour deposition method that significantly enhanced PEC water splitting performance.²⁰ The photocurrent density of WO₃ increases by more than a factor of nine upon coupling with α -Fe₂O₃, as reported by Mao *et al.*²¹ In addition, Xia *et al.* demonstrated that α -Fe₂O₃/BiVO₄ heterojunction photoanodes greatly enhanced PEC performance.²² Another promising

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approach for improvement of charge separation is the formation of $n-n$ type heterostructures, which can facilitate more optimal charge transport properties and separation as well as limit electron/hole (e^-/h^+) recombination. Recently, $n-n$ type heterostructures such as CdS/FST,²³ BiVO₄/CdS,²⁴ WO₃/Fe₂O₃,²⁵ and WO₃/ZnWO₄ have been used for PEC water splitting.²⁶

Among the various $n-n$ type heterostructure semiconductors, ZnWO₄ has emerged as an attractive second semiconductor due to its suitable conduction band position, satisfactory electron mobility, and excellent chemical stability. In particular, because of its high stability in acidic and alkaline media, along with strong interfacial superior compatibility with oxide semiconductors, ZnWO₄ is highly suitable for constructing heterojunction photoanodes.^{27,28} For example, the formation of a WO₃/ZnWO₄ heterojunction photoanode is effective for increasing the visible light absorption and charge separation efficiency because ZnWO₄ possesses a wide range of band gaps, $E_g \approx 3.2-3.8$ eV.²⁹⁻³¹ Moreover, these synthesis methods and conventional annealing techniques are complex, and controlling surface morphology is difficult.³²

Conventional thermal annealing often leads to severe crystal sintering and damage to the fluorine-doped tin oxide (FTO) glass substrate. In contrast, hybrid microwave annealing enables high-temperature crystallization while effectively suppressing sintering and preserving FTO integrity, as demonstrated for Fe₂O₃, CuFeO₂, CuO, ZnFe₂O₄, and Fe₂TiO₅.^{33,34} There are very few research articles available on photoelectrode preparation using an easy and inexpensive synthesis procedure for PEC water splitting applications.

In this research, we employed an α -Fe₂O₃/ZnWO₄ heterojunction photoanode prepared by the simple method of hydrothermal treatment with a hybrid microwave annealing approach, and the improvement of PEC water oxidation resulting from the formation of an α -Fe₂O₃/ZnWO₄ heterostructured photoanode was systematically studied. The recorded research shows that the α -Fe₂O₃/ZnWO₄ heterojunction photoanode reached maximum photocurrent density at the potential of 1.23 V (vs. reversible hydrogen electrode (RHE)) as compared to that of the value recorded for pure α -Fe₂O₃. The absorption of visible light of α -Fe₂O₃/ZnWO₄ was redshifted as compared to that of α -Fe₂O₃. This resulted in enhanced visible spectrum photon absorption, which in turn affected the increase in photocurrent density attained for the α -Fe₂O₃/ZnWO₄ heterojunction photoanode. Also, the formation of the α -Fe₂O₃/ZnWO₄ heterojunction photoanode produced an additional electric field at the $n-n$ junction that was greatly decreased by the recombination of electron-hole pairs and facilitated the mobility of photoexcited charge carriers. The morphology of ZnWO₄ deposited on α -Fe₂O₃ to form the heterostructure was bundled nanosheets, which played an important role in increasing charge separation, and consequently increased the applied bias photon-to-current efficiency (ABPE). To the best of our knowledge, we report for the first time the synthesis of an α -Fe₂O₃/ZnWO₄ $n-n$ heterojunction photoanode by a hybrid microwave annealing technique. The overall PEC water oxidation performance of the α -Fe₂O₃/ZnWO₄ $n-n$

heterojunction is discussed in the results and discussion section.

2. Materials and methods

FTO (fluorine-doped tin oxide) glass substrate (resistivity approximately 7 Ω /sq) was purchased from Sigma-Aldrich. Sodium tungstate (Na₂WO₄·2H₂O) (assay 96%) (Nice Chemicals), iron(III) chloride (FeCl₃·6H₂O) (98% pure) (Sigma-Aldrich), [Zn(NO₃)₂·2H₂O] (assay 98%) (Molychem), ethanol AR (analytical grade) 99.9%, and hydrochloric acid were obtained for synthesis use. The complete chemical reagents were used without any further purification. Double distilled (DD) water was used as a solvent throughout the photoanode preparation.

2.1. Preparation of the α -Fe₂O₃ photoanode

A hydrothermal method was used to synthesize the α -Fe₂O₃ nanorod photoanode. The first 50 mL of a mixed solution consisting of 15% water, 35% ethanol, and 3% acetic acid with 0.1 M FeCl₃·6H₂O was stirred for 30 min. The transparent solutions obtained were then transferred into a 50 mL autoclave with the FTO glass substrate (wall side facing down), and then processed with a hydrothermal treatment at 120 °C for 4 h. Then, the FeOOH films were cleaned with DD water, dried, and annealed at 700 °C for 5 min by hybrid-microwave annealing to obtain the α -Fe₂O₃ photoanode.

2.2. Preparation of the α -Fe₂O₃/ZnWO₄ photoanode

First, 0.25 mM of [Zn(CH₃COO)₂·2H₂O] was dissolved in 50 mL of DD water and then added to 0.25 mM of [Na₂WO₄·2H₂O] and stirred for 30 min, which yielded a transparent solution. The precursor solution was sealed in a 50 mL autoclave and maintained at 180 °C for 3 h. Finally, the obtained samples were then annealed at 550 °C for 15 min using hybrid microwave annealing and marked as α -Fe₂O₃/ZnWO₄. Fig. 1 shows a schematic of the formation process for the α -Fe₂O₃/ZnWO₄ heterojunction photoanode.

2.3. Material characterization

The morphology of the prepared photoanodes was analyzed by scanning electron microscopy (SEM) (SIGMA with Gemini Column, Carl Zeiss, USA). The elemental composition was confirmed by energy-dispersive X-ray spectrometry (EDS) using a Bruker (German) Nano XFlash Detector. The phase formation was determined by X-ray diffraction (XRD) analysis with Cu-K α radiation, $\lambda = 1.5406$ Å, using a RigakuD/Max Ultima3i diffractometer. A UV-Vis double beam spectrometer (INFR DIGI IR-513D) was used to record light absorption between 200 and 800 nm.

2.4. PEC studies

The complete PEC measurements of the as-prepared photoanodes were examined in a standard three-electrode setup using an electrochemical workstation (BioLogic SP-150), with



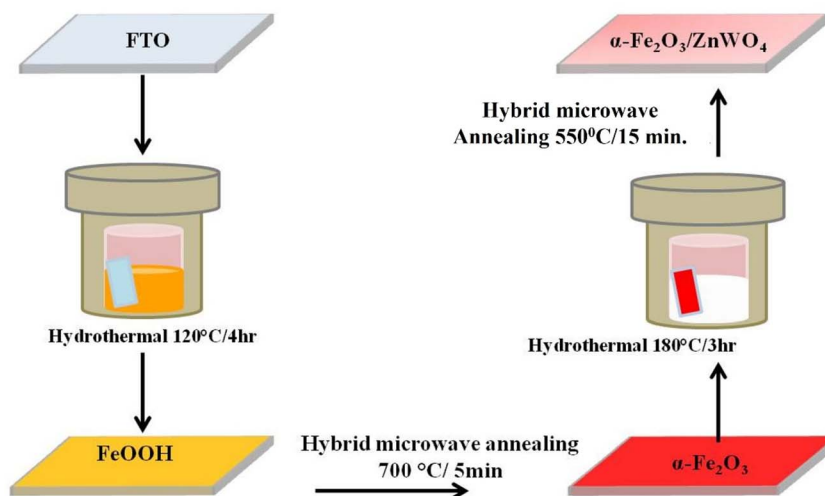


Fig. 1 A schematic diagram showing the preparation of an α -Fe₂O₃/ZnWO₄ heterojunction.

the α -Fe₂O₃/ZnWO₄ *n-n* heterojunction-based photoanode, Ag/AgCl in saturated KCl, and a platinum sheet as the working, reference, and counter electrodes, respectively. The electrolyte used was a 1 M NaOH aqueous solution. In experiments, a 150 W xenon lamp (GLORIA-X-150A) acted as the light source with an AM 1.5 G filter, with the intensity of the light at 100 mW cm⁻². Linear sweep voltammetry (LSV) measurements were performed at a scan rate of 10 mV s⁻¹. The chronoamperometric curves were recorded in 1 M NaOH at 1.23 V vs. RHE.

The electrochemical impedance spectroscopy (EIS) study was performed with a frequency range of 1–100 kHz. During the PEC measurements, the working electrode potential (vs. Ag/AgCl) was changed to be a scale of the RHE using the Nernst equation:^{35,36}

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.059 (\text{pH}) + E^0_{\text{Ag/AgCl}} \quad (1)$$

where $E_{\text{Ag/AgCl}}$ indicates an experimentally measured potential against the Ag/AgCl electrode, $E^0_{\text{Ag/AgCl}} = 0.1976$ V at 25 °C, and E_{RHE} denotes converted potential.

3. Results and discussion

Fig. 2 displays the top view FE-SEM images of the α -Fe₂O₃, ZnWO₄, and α -Fe₂O₃/ZnWO₄ photoanodes. According to the vertical (top) view FE-SEM images, the α -Fe₂O₃ appears as highly ordered and well aligned nanorods, with an average diameter of 50 ± nm after being grown on FTO film (Fig. 2a). As shown in Fig. 2b, the ZnWO₄ photoanode exhibits a petal-like morphology with an average length of approximately 85 ± 5 nm. The heterostructured α -Fe₂O₃/ZnWO₄ film (Fig. 2c) displays a mixed morphology, where ZnWO₄ nanoparticles are uniformly dispersed over the α -Fe₂O₃ nanorod.

This morphology suggests successful integration of both materials, which promotes the formation of heterojunctions favorable for enhanced charge separation and transport. Furthermore, the elemental composition was verified through

EDS analysis (Fig. 2d), which confirmed the presence of Fe, Zn, W, and O, thus supporting the formation of the α -Fe₂O₃/ZnWO₄ heterostructured photoanode. The Sn signal originates from the FTO substrate. The absence of any impurity peaks indicates the high purity of the prepared heterostructure. The quantitative analysis of the composition is listed in Table 1.

To increase our understanding of the structure of α -Fe₂O₃/ZnWO₄, its microstructural features were examined by transmission electron microscopy (TEM), as shown in Fig. 2e and f. The low-magnification TEM image (Fig. 2e) demonstrates that the composite consists of aggregated nanostructures with intimate interfacial contact between the two semiconductors. The high-magnification TEM image (Fig. 2f) further reveals closely packed heterostructured domains at the nanoscale, indicating satisfactory dispersion of ZnWO₄ within the α -Fe₂O₃ matrix. Noticeably, the high-resolution transmission electron microscopy (HRTEM) image (Fig. 2g) shows well-resolved lattice fringes with interplanar spacings of 0.253 nm and 0.241 nm, which can be indexed to the (110) plane of α -Fe₂O₃ and the (021) plane of ZnWO₄, respectively. This clearly confirms the interface between the Fe₂O₃ nanorods and the ZnWO₄ heterojunction.

The corresponding SAED pattern (Fig. 2h) exhibits a series of concentric diffraction rings composed of bright spots, demonstrating the polycrystalline nature of the heterojunction. The diffraction rings can be indexed to the characteristic crystal planes of α -Fe₂O₃ and ZnWO₄, which is in agreement with the XRD results and further confirms the existence of both crystalline phases. Thus, it is evidenced that the formation of the α -Fe₂O₃/ZnWO₄ heterojunction occurred.

The XRD patterns of ZnWO₄, α -Fe₂O₃, and the α -Fe₂O₃/ZnWO₄ heterojunction are shown in Fig. 3. Fig. 3a shows the XRD patterns of FTO, and ZnWO₄ synthesized at 500 °C (Zn 500), 550 °C (Zn 550), and 600 °C (Zn 600). The most prominent high-intensity peaks marked with red asterisks (*) appear from the FTO substrate related to the SnO₂ characteristic peaks, while the peaks corresponding to monoclinic ZnWO₄ are denoted by black hearts (♥). Among the three, the ZnWO₄



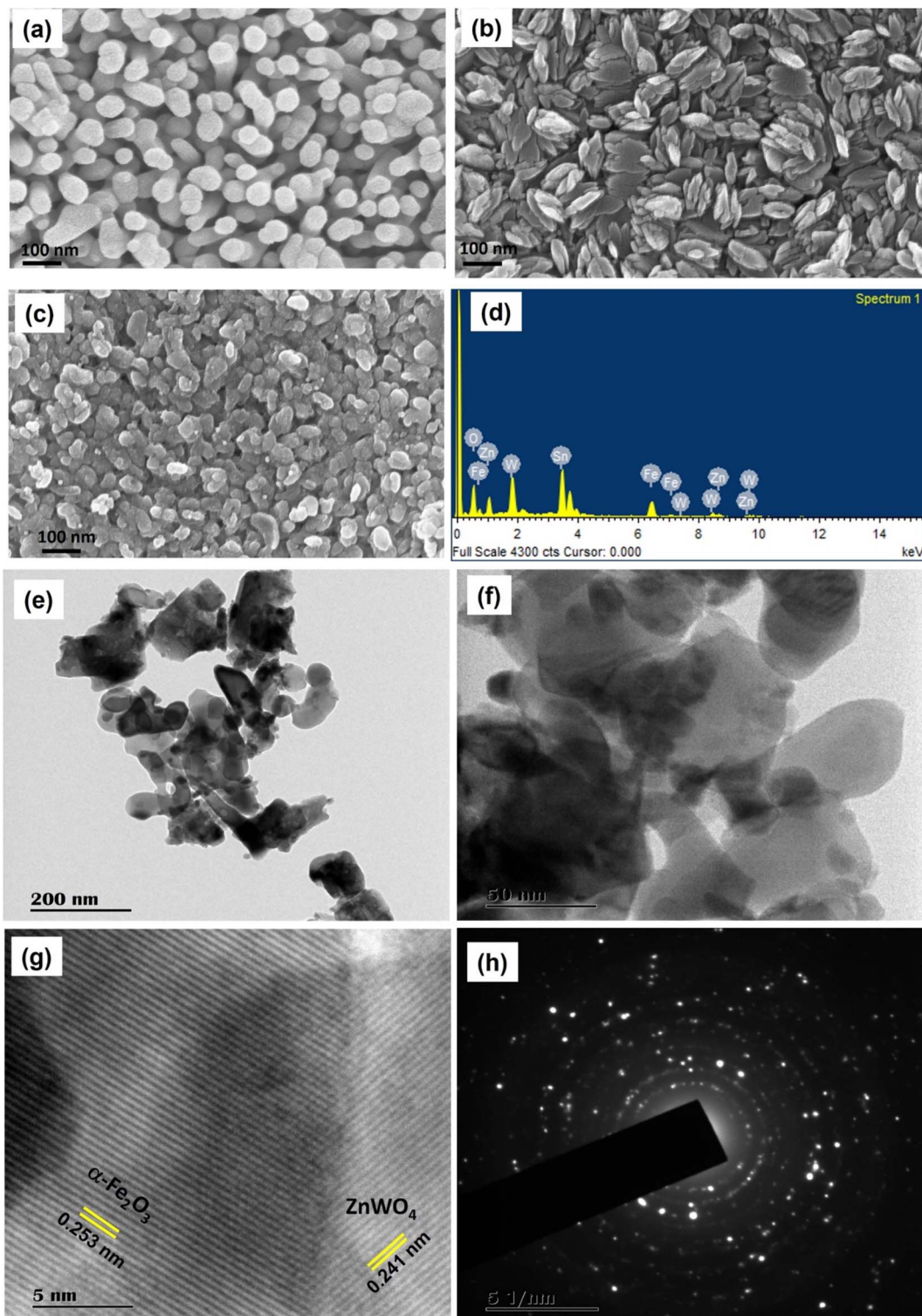


Fig. 2 FESEM images of (a) α -Fe₂O₃, (b) Zn 550, and (c) α -Fe₂O₃/ZnWO₄, (d) EDS spectrum and (e–h) HR-TEM images of the α -Fe₂O₃/ZnWO₄ heterostructure.

sample annealed at 550 °C (Zn 550) exhibits the sharpest and most intense ZnWO₄ diffraction peaks, indicating enhanced crystallinity compared to the 500 °C and 600 °C samples.

The lower crystallinity at 500 °C is due to incomplete phase formation, while peak broadening at 600 °C is due to thermally

induced lattice strain. Hence, 550 °C is the optimal annealing temperature for ZnWO₄. The major diffraction peaks of ZnWO₄ appear at 15.43°, 18.75°, 23.9°, 31.2°, 36.2°, 47.7°, 48.7°, and 68.2°, which correspond to the (010), (100), (001), (020), (021), (030), (022), and (041) crystal planes, respectively. These peaks



Table 1 EDX elemental compositional analysis of α -Fe₂O₃/ZnWO₄

Composition	Sn	O	Fe	Zn	W
Weight%	33.01	34.08	10.33	3.66	18.92
Atomic%	10.11	77.40	6.72	6.72	3.74

match well with the standard data for ZnWO₄, confirming its formation in the monoclinic crystal system (JCPDS: 15-0774).³⁷

As for α -Fe₂O₃, there are two diffraction peaks located at 35.6° and 64.2°, which correspond to the (110) and (300) planes of the rhombohedral crystal phase of α -Fe₂O₃ (JCPDS: 33-0664) (Fig. 3b).³¹ In the α -Fe₂O₃/ZnWO₄ heterojunction, peaks for ZnWO₄ and α -Fe₂O₃ are observed, indicating successful formation of the heterojunction. However, the disappearance of the low-intensity ZnWO₄ peak at 15.43° in the heterojunction photoanode is due to the reduced crystallite size, interfacial strain, and partial peak overlap with α -Fe₂O₃, all of which suppress its detectability.

UV-visible spectroscopy was performed to understand the light-absorption mechanisms of the α -Fe₂O₃/ZnWO₄ heterojunction photoanode, which ranges in wavelength from 400 to 800 nm (Fig. 4a). It is clearly shown that the light absorption edge of the α -Fe₂O₃/ZnWO₄ photoanode significantly redshifted when compared to ZnWO₄ and α -Fe₂O₃, which is due to the formation of the heterojunction.^{38,39} The bandgap can be estimated using a Tauc plot, which is shown in Fig. 4b. According to the Tauc result, the band gap of monoclinic ZnWO₄ was estimated to be 3.2 eV, while that of α -Fe₂O₃ was 2.02 eV. The α -Fe₂O₃/ZnWO₄ heterojunction exhibited a slightly increased band gap of 2.2 eV, indicating a shift due to the interfacial electronic interaction between the two semiconductors.^{29,31}

X-ray photoelectron spectroscopy (XPS) was conducted to examine the elemental composition and chemical states of the α -Fe₂O₃/ZnWO₄ heterojunction photoanode. The survey spectrum (Fig. 5a) confirms the presence of Fe, Zn, W, O, and Sn elements, revealing the successful composition of the heterojunction. In Fig. 5b, the high-resolution Fe 2p spectrum exhibits

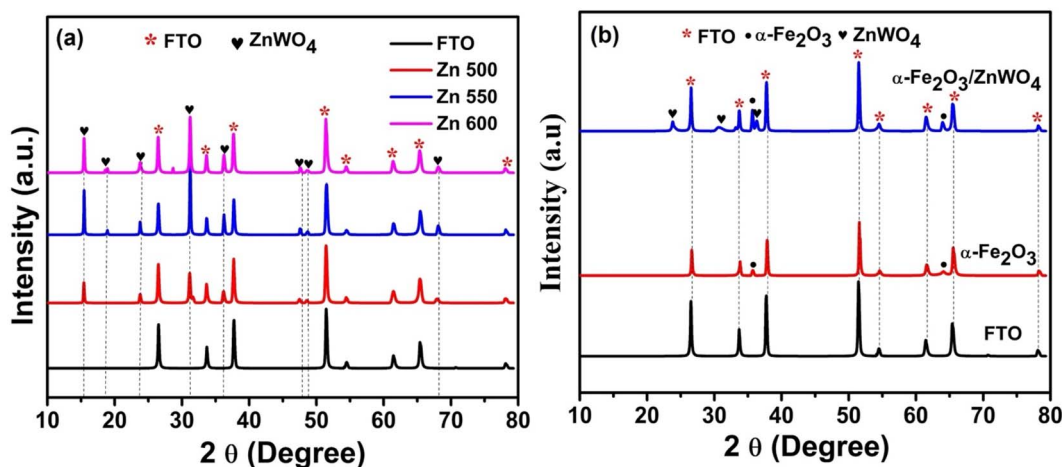


Fig. 3 XRD patterns of (a) ZnWO₄ annealed at different temperatures and the (b) Zn 550, α -Fe₂O₃, and α -Fe₂O₃/ZnWO₄ heterojunction photoanodes.

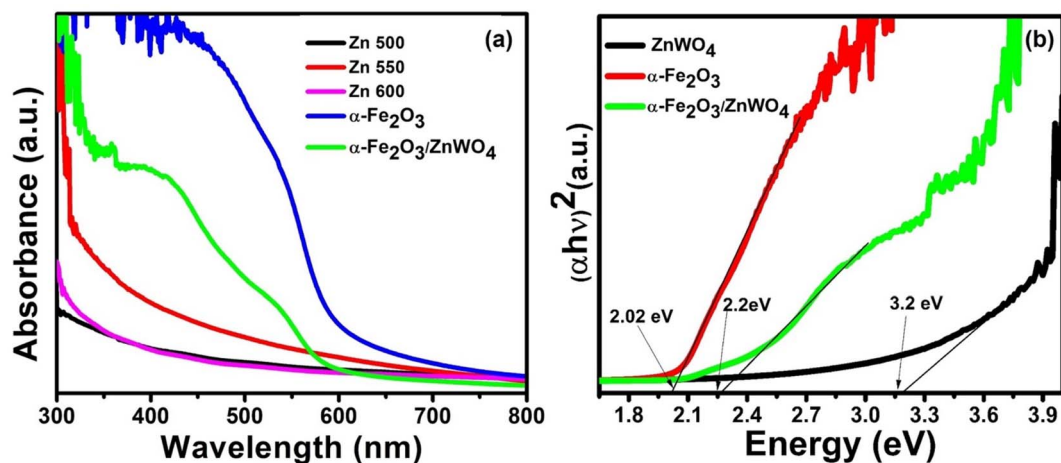


Fig. 4 (a) UV-Vis spectrum and (b) Tauc plot of the ZnWO₄, α -Fe₂O₃, and α -Fe₂O₃/ZnWO₄ heterojunction photoanodes.



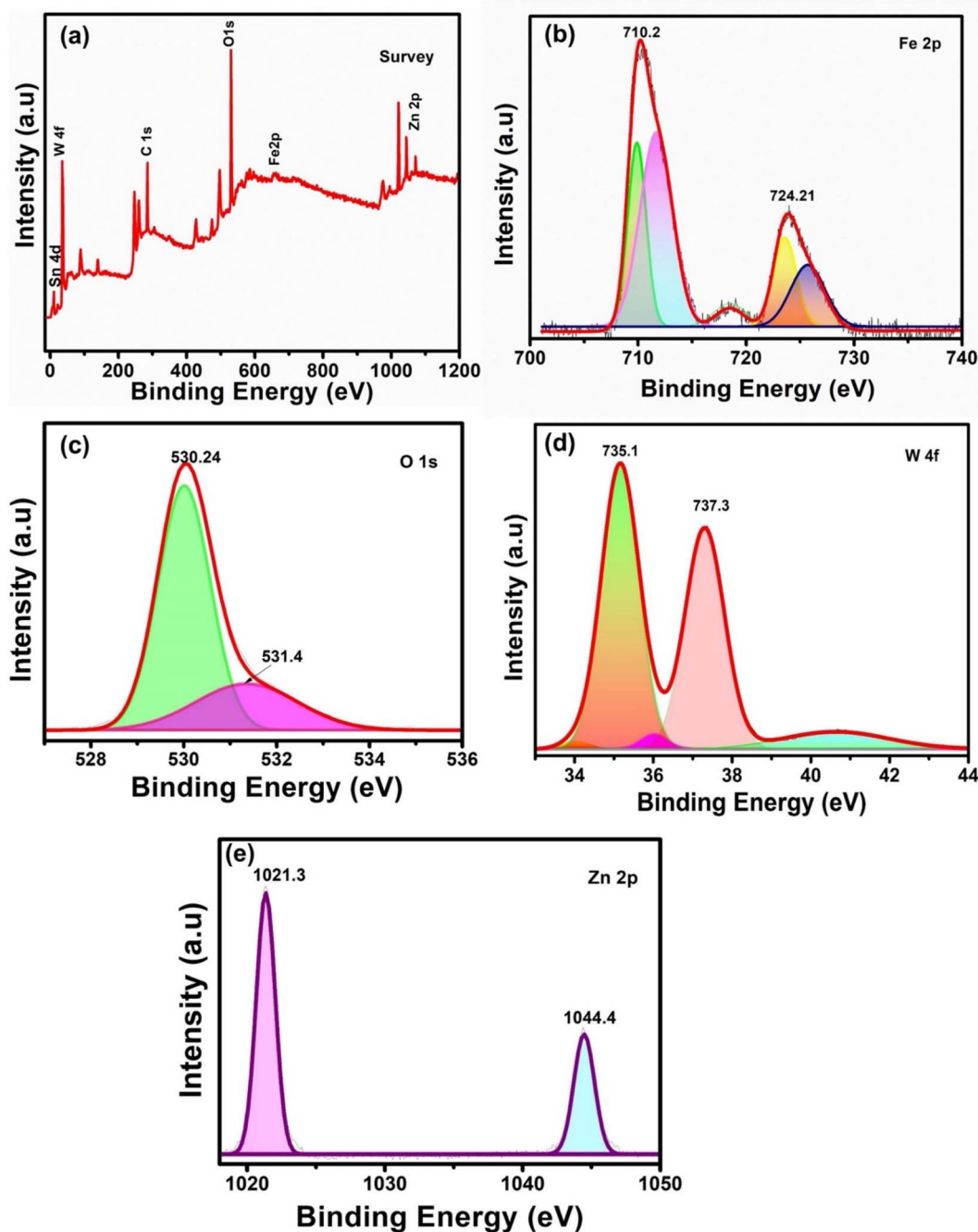


Fig. 5 XPS spectra of the α -Fe₂O₃/ZnWO₄ (a) survey, (b) Fe 2p, (c) O 1s, (d) Zn 2p, and (e) W 4f.

two prominent peaks corresponding to Fe 2p_{3/2} and Fe 2p_{1/2}, located at 710.2 eV and 724.21 eV, respectively.

It is well known that the core-level binding energy of an element increases with an increasing valence (oxidation) state, due to the enhanced effective nuclear charge experienced by the core electrons. In the case of iron oxides, this trend is clearly reflected in the Fe 2p spectra. The Fe 2p_{3/2} binding energy is typically located at approximately 709 eV for Fe²⁺ species, while it shifts to higher binding energies (710–711 eV) for Fe³⁺ species. In the present α -Fe₂O₃/ZnWO₄ photoanode, the Fe 2p_{3/2} peak appears at 710.2 eV. In addition, the binding energy of a distinct

shake-up satellite peak was observed at 718.6 eV, which is fully consistent with the Fe³⁺ oxidation state in the α -Fe₂O₃ phase, as previously reported.⁴⁰

The O 1s spectrum (Fig. 5c) shows two deconvoluted peaks at 530.24 eV and 531.4 eV.³⁹ The lower binding energy peak was attributed to lattice oxygen (O²⁻), while the higher binding energy peak was attributed to surface-adsorbed oxygen or hydroxyl species. Surface oxygen species are beneficial for PEC activity by favoring charge separation and surface reaction.

The W 4f spectrum (Fig. 5d) shows peaks at 35.1 eV and 37.3 eV, which were attributed to W 4f_{7/2} and W 4f_{5/2},



respectively. The two peaks are associated with the photoelectrons emitted from W atoms in the W^{6+} oxidation state, which agrees with the report of $ZnWO_4$. Furthermore, there was a spin orbit separation of approximately 2.2 eV, which is consistent with W^{6+} species in $ZnWO_4$. No additional peaks corresponding to reduced tungsten species (W^{5+} or W^{4+}) were detected, suggesting that tungsten exclusively exists in the W^{6+} oxidation state. This confirms the formation of stoichiometric $ZnWO_4$ and its stable integration with $\alpha\text{-Fe}_2\text{O}_3$. Fig. 5e displays the Zn 2p spectrum, which includes two peaks at 1021.3 eV and 1044.4 eV, corresponding to Zn 2p_{3/2} and Zn 2p_{1/2}, respectively. The peaks indicate the 2+ oxidation state of Zn in $ZnWO_4$. The existence of a distinct Zn 2p peak also supports the successful integration of $ZnWO_4$ with $\alpha\text{-Fe}_2\text{O}_3$.⁴¹

The PEC behavior and interfacial charge transport properties of Zn 550, $\alpha\text{-Fe}_2\text{O}_3$, and their heterojunction ($\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$) were systematically evaluated, and are shown in Fig. 6. Fig. 6a shows the photocurrent density (J - V) curves for $ZnWO_4$ thin films annealed at different temperatures (500 °C, 550 °C, and 600 °C). The $ZnWO_4$ sample annealed at 550 °C exhibited the highest photocurrent density, indicating an optimal crystalline structure and enhanced photoactivity at this temperature. Fig. 6b shows the photocurrent response of pristine Zn 550, pristine $\alpha\text{-Fe}_2\text{O}_3$, and their heterostructure ($\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$) under solar illumination. Among the three, the heterojunction

exhibited significantly enhanced photocurrent density, reaching 0.86 mA cm^{-2} at 1.23 V vs. RHE, which is much higher than pristine $\alpha\text{-Fe}_2\text{O}_3$ (0.29 mA cm^{-2}) or Zn 550 (0.05 mA cm^{-2}), while the corresponding photocurrent measurements recorded in the presence of H_2O_2 are provided in Fig. S1. This is due to the enhanced charge separation and decreased recombination caused by the favorable band alignment in the heterojunction.

The black solid circle shows that the dark current of $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ is steady and approximately zero. These indicate that the photoexcited carriers are crucial to the generation of photocurrent, and the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction obviously enhanced the photoexcited carriers, which significantly accelerated the PEC water oxidation.⁴² Table S1 summarizes the $\alpha\text{-Fe}_2\text{O}_3$ -based heterojunction photoanodes and their corresponding PEC performance (photocurrent density at 1.23 V vs. RHE mA cm^{-2}). Furthermore, the efficiency of charge injection (η_{inj}) and charge separation (η_{sep}) were determined by the following formulas:^{43,44}

$$\eta_{\text{inj}} = J_{\text{H}_2\text{O}}/J_{\text{H}_2\text{O}_2} \quad (2)$$

$$\eta_{\text{sep}} = J_{\text{H}_2\text{O}_2}/J_{\text{abs}} \quad (3)$$

where $J_{\text{H}_2\text{O}}$ and $J_{\text{H}_2\text{O}_2}$ denote photo-water oxidation and hole scavenger, respectively.

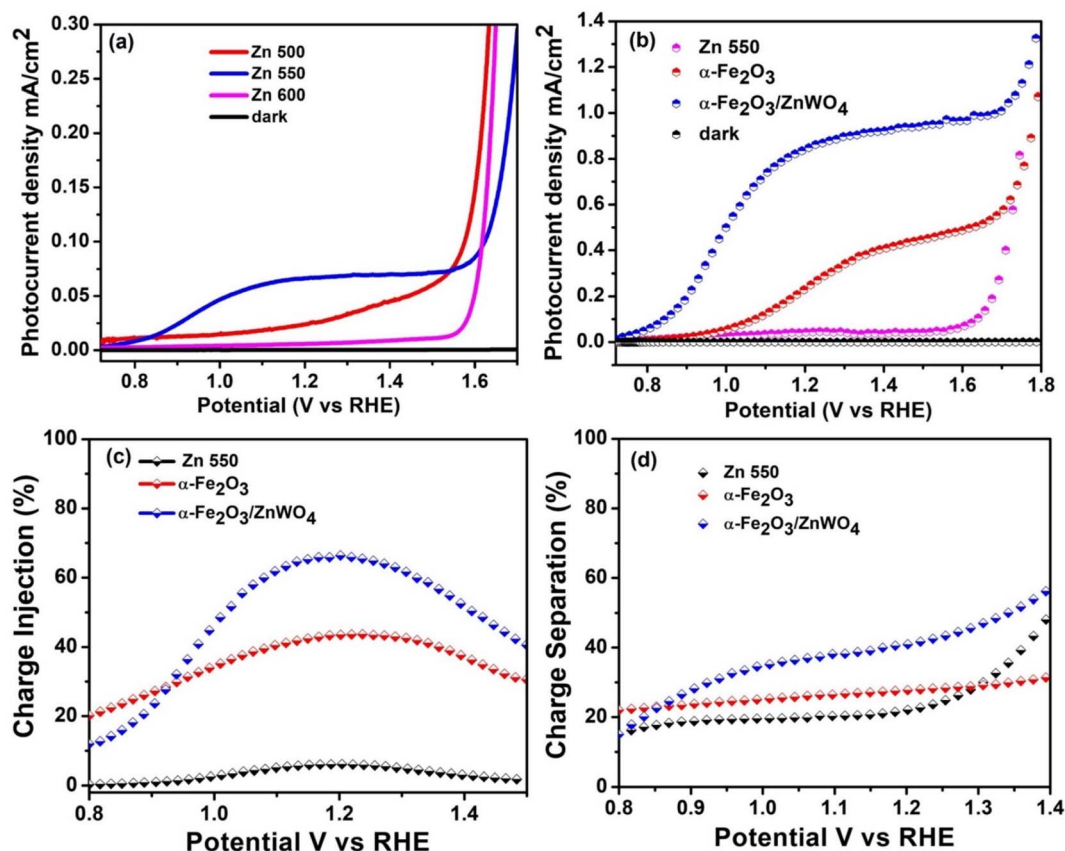


Fig. 6 (a) LSV plots of $ZnWO_4$ annealed at different temperatures. (b) LSV plots. (c) Charge injection and (d) charge separation of the Zn 550, $\alpha\text{-Fe}_2\text{O}_3$, and $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanodes.



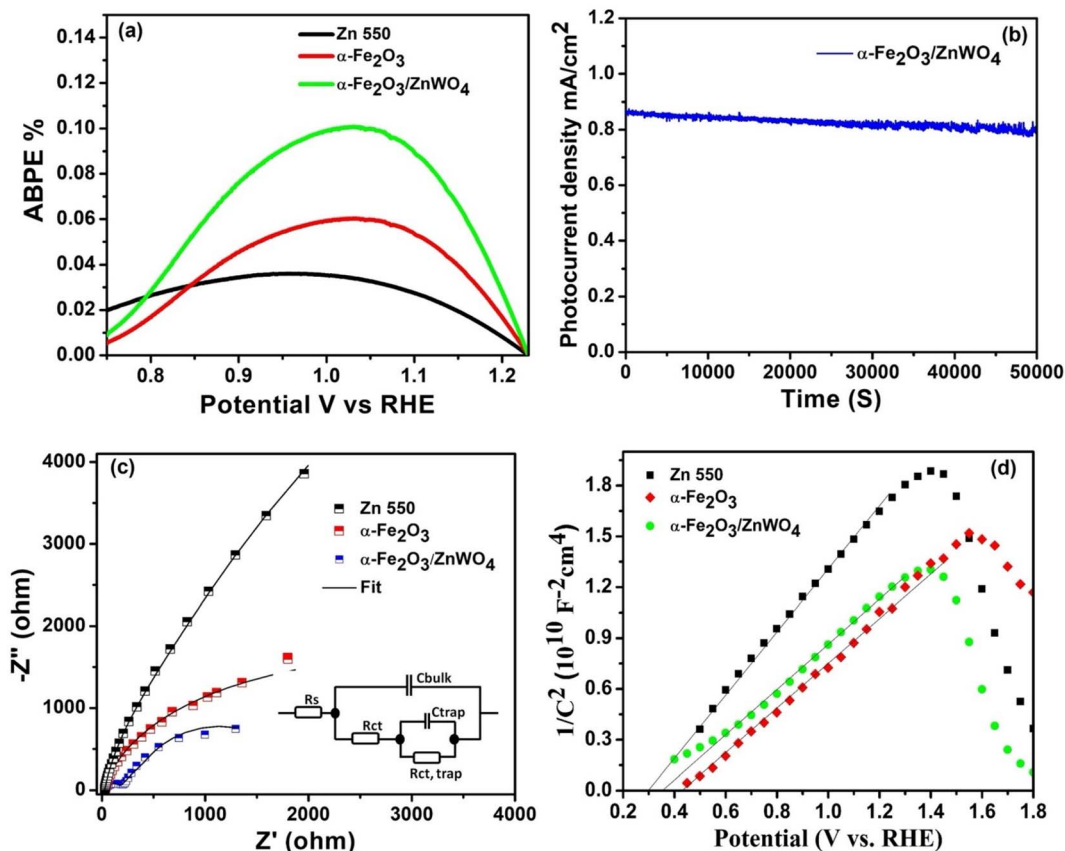


Fig. 7 (a) ABPE, (b) long-term chronoamperometry, (c) Nyquist plots, with the inset showing the equivalent circuit model, and (d) Mott–Schottky plots of the Zn 550, α -Fe₂O₃, and α -Fe₂O₃/ZnWO₄ photoanodes.

Fig. 6c presents the calculated charge injection efficiency as a function of applied potential. The α -Fe₂O₃/ZnWO₄ photoanode showed the highest injection efficiency across the entire potential range, peaking at approximately 66.16% at 1.2 V vs. RHE. This suggests that the heterostructure facilitates more efficient hole transfer from the semiconductor to the electrolyte compared to the individual components. Hence, the satisfactory interface injection between α -Fe₂O₃/ZnWO₄ and the electrolyte significantly accelerated the water oxidation process. The charge separation of α -Fe₂O₃/ZnWO₄ reached 42.51% at 1.23 V vs. RHE, which is more than that of α -Fe₂O₃ (28.30%) and Zn 550 (17.82%), as shown in Fig. 6d. These results confirm that the formation of a heterojunction effectively suppresses bulk recombination and improves carrier mobility.^{45,46}

As shown in Fig. 7a, the calculated ABPE value of the α -Fe₂O₃/ZnWO₄ heterojunction photoanode is higher than that of the pure Zn 550 and α -Fe₂O₃ photoanodes (Table 2). The results

Table 2 Calculated η_{inj} and η_{sep} efficiencies and ABPE values

Photoanode material	η_{inj} (%)	η_{sep} (%)	ABPE (%)
Zn 550	6.45	17.82	0.033
α -Fe ₂ O ₃	43.82	28.30	0.060
α -Fe ₂ O ₃ /ZnWO ₄	66.13	42.51	0.10

demonstrate that the separation efficiency of the α -Fe₂O₃/ZnWO₄ heterojunction has significantly improved, with greater solar conversion efficiency for PEC water oxidation. The following ABPE calculations were obtained according to previously reported work.^{47,48}

A long-term chronoamperometry test for over 50 000 seconds for α -Fe₂O₃/ZnWO₄ under constant illumination shows a stable photocurrent density of approximately 0.86 mA cm⁻², with minimal decay (Fig. 7b). This result confirms the structural stability and resistance to photocorrosion of the heterostructure, which is critical for practical PEC applications.⁴⁹ Furthermore, the reproducible and rapid photocurrent response observed during chopped light on/off conditions demonstrates the fast charge separation and transport, as well as the satisfactory photoresponse reversibility of the α -Fe₂O₃/ZnWO₄ photoanode, as shown in Fig. S2.⁵⁰

Further insight into the interfacial charge-transfer kinetics of the Zn 550, α -Fe₂O₃, and α -Fe₂O₃/ZnWO₄ heterojunctions was obtained by electrochemical impedance spectroscopy (EIS) measurements with fixed bias potential and frequency of 1 Hz to 100 kHz. The charge-transfer resistance and capacitance values of the Zn 550, α -Fe₂O₃, and α -Fe₂O₃/ZnWO₄ heterojunction photoanodes were fitted by the EIS data using an equivalent circuit model (Z fit model), as shown in Fig. 7c, and their corresponding equivalent circuit is shown in the inset in Fig. 7c.^{51,52}



Table 3 The fitted EIS results

Photoanode	R_s (ohm cm^{-2})	R_2 (ohm cm^{-2})	R_{ct} (ohm cm^{-2})	C_1 ($\mu\text{F cm}^{-2}$)	C_2 ($\mu\text{F cm}^{-2}$)
Zn 550	36.8	860.3	645.2	0.582	4.23
$\alpha\text{-Fe}_2\text{O}_3$	35.13	532.9	290.1	0.825	5.38
$\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$	30.19	143.1	52.8	3.783	15.26

Table 4 Parameters from Mott–Schottky plots for the $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ photoanodes

Photoanode	Donor density (cm^{-3})	Flatband potential
Zn 550	0.0067×10^9	0.30
$\alpha\text{-Fe}_2\text{O}_3$	0.152×10^9	0.43
$\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$	0.147×10^{12}	0.35

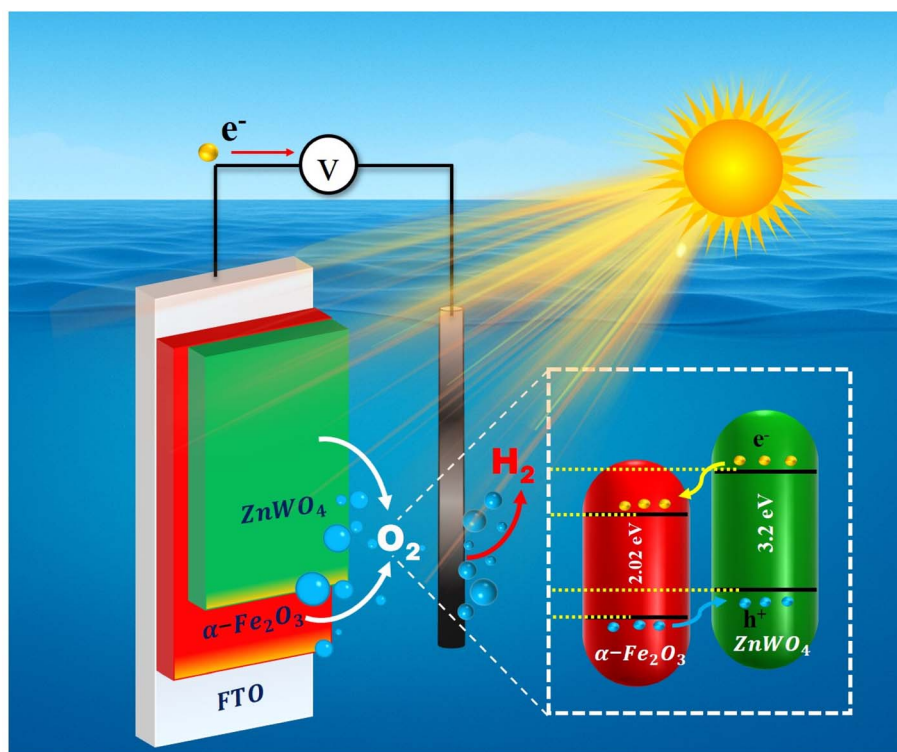
In this Z fit model, R_s denotes all the series resistance in the PEC cell, including the resistance of the FTO substrate.⁵³ The R_{trap} denotes the charge trapping resistance in the bulk semiconductor photoelectrode, and R_{ct} represents the charge-transfer resistance across the bulk/electrolyte interface.⁵⁴ In addition, C_{bulk} and C_{trap} reflect the space-charge capacitance of the bulk and Helmholtz capacitance at the photoanode/electrolyte interface, respectively.⁵⁵ However, the fitting values of R_{trap} and R_{ct} for the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode are significantly decreased (Table 3) compared to those of the pristine $\alpha\text{-Fe}_2\text{O}_3$ and ZnWO_4 photoanodes, which indicates that the surface trapping and transfer of photogenerated holes

in the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode is much easier than that in the $\alpha\text{-Fe}_2\text{O}_3$ and ZnWO_4 photoanodes. The EIS results clearly demonstrate the formation of the ZnWO_4 heterojunction on $\alpha\text{-Fe}_2\text{O}_3$, which can significantly promote the surface charge transfer during the water oxidation reaction and accelerate the separation of $(e^-)/(h^+)$.

The Mott–Schottky plots of the $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanodes were created to understand the semiconductor type (Fig. 7d). The carrier density and flat band potential were calculated using the Mott–Schottky equation:^{56,57}

$$1/C^2 = 2/\epsilon \epsilon_0 e N_D [(V - V_{\text{FB}}) - kT/e] \quad (4)$$

where C denotes the specific capacitance, V denotes the applied bias potential of the $\alpha\text{-Fe}_2\text{O}_3$ photoelectrode, V_{FB} denotes the flat band potential, kT/e specifies the term of temperature-dependent correction, e denotes the charge of the electron, N_D denotes the electron density, and ϵ , ϵ_0 denote the represented dielectric constant and permittivity of vacuum of $\alpha\text{-Fe}_2\text{O}_3$, respectively. The positive slope of the $\alpha\text{-Fe}_2\text{O}_3$ and $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanodes suggests that they are n-

Fig. 8 Proposed mechanism of the charge transfer of an $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode.

type semiconductor materials. The V_{FB} and a donor density of both photoanodes are listed in Table 4. The donor density of the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction is 0.147×10^{12} , which is much greater than that of pure Zn 550 and $\alpha\text{-Fe}_2\text{O}_3$. Therefore, the staggered $n\text{-}n$ heterojunction is beneficial for additional electronic properties in $\alpha\text{-Fe}_2\text{O}_3$ films and satisfactory PEC water oxidation performance.

The proposed charge transfer and reaction mechanism of the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode under solar illumination are shown in Fig. 8. Upon light excitation, $\alpha\text{-Fe}_2\text{O}_3$ and ZnWO_4 absorb incident photons and generate electron-hole (e^-/h^+) pairs. Because of the favorable band alignment between $\alpha\text{-Fe}_2\text{O}_3$ ($E_g \approx 2.02$ eV) and ZnWO_4 ($E_g \approx 3.2$ eV), the photogenerated electrons in the conduction band (CB) of ZnWO_4 are driven toward the conduction band of $\alpha\text{-Fe}_2\text{O}_3$, while the holes remain in the valence band (VB) of ZnWO_4 . The CB and VB positions of $\alpha\text{-Fe}_2\text{O}_3$ and ZnWO_4 were estimated based on previously reported work.⁵⁸ The CB and VB edges of $\alpha\text{-Fe}_2\text{O}_3$ are located at +0.37 V and +2.39 V vs. NHE, respectively, with an electron affinity (χ) of approximately 5.88 eV, while ZnWO_4 exhibits a CB position at +0.21 V, a VB position at +3.41 V vs. RHE, and an electron affinity (χ) of approximately 6.31 eV.^{59,60}

The accumulated holes on the valence band of ZnWO_4 possess sufficient oxidation potential to drive the oxygen evolution reaction (OER), leading to the generation of O_2 from water oxidation at the photoanode surface. Simultaneously, the transferred electrons in the conduction band of $\alpha\text{-Fe}_2\text{O}_3$ are transported through the FTO substrate and the external circuit towards the counter electrode, where they participate in the hydrogen evolution reaction (HER) to produce H_2 . Thus, the formation of the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ $n\text{-}n$ type heterojunction significantly enhanced the charge separation efficiency, accelerated the interfacial charge transfer, and improved the overall PEC water-splitting performance.

4. Conclusion

We designed an $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode for PEC water splitting. The formation of a heterojunction between $\alpha\text{-Fe}_2\text{O}_3$ and a ZnWO_4 nanostructured array significantly increased the photocurrent density by 2.2-fold. Moreover, there was a higher ABPE value (0.10%) for the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction. This could be due to the improved light absorption as well as the improved transport properties of the $\alpha\text{-Fe}_2\text{O}_3/\text{ZnWO}_4$ heterojunction photoanode.

More specifically, the ZnWO_4 hole storage layer effectively reduced the transport charge resistance so that holes were stored in the ZnWO_4 heterojunction layer, resulting in enhanced electron-hole separation efficiency. This work demonstrates a method for fabricating highly active heterojunction photoanodes by hybrid microwave annealing that is an emerging and noticeably viable route to improve PEC performance.

Conflicts of interest

There are no conflicting interests.

Data availability

The data presented in this article are available from the corresponding author on reasonable request.

Supplementary information (SI) is available. See DOI: <https://doi.org/10.1039/d5ra07601c>.

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