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Interface engineering Z-scheme Ti-Fe₂O₃/In₂O₃ photoanode for highly efficient photoelectrochemical water splitting

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ABSTRACT

Exploiting interface-engineer of In_2O_3 -based photoanode to achieve a higher charge separation efficiency could be regarded as a pivotal but challenging research in water splitting. Herein, the state-of-the-art Ti-Fe₂O₃/In₂O₃ photoanodes with different Ti⁴⁺ doping concentrations are fabricated for exploring the interface-engineering effect on PEC performance. The optimized 150Ti-Fe₂O₃/In₂O₃ photoelectrode with the rapid interfacial hole trapped (~ 8.96 ps) and long-lived charge separation states could achieve excellent PEC performance by femtosecond time-resolved absorption spectroscopy (fs-TAS). As expected, it shows the highest photocurrent density of 2 mA/cm² at 1.23 V vs. RHE, which is nearly 7 times higher compared with pure In₂O₃. Moreover, the Z-scheme mechanism could be fully confirmed by femtosecond time-resolved absorption spectroscopy (fs-TAS) and in-situ double-beam detection strategy (AM 1.5 + 405 nm). This work provides an effective and feasible strategy on designing and regulating high-efficiency composite photoanode with Z-scheme transfer mechanism.

1. Introduction

Water oxidation is deemed as the primary reaction of photoelectrochemistry (PEC) water splitting to largely achieve the solar energy conversion [1,2]. Therefore, designing excellent photoanode to optimize water oxidation process has been regarded as the priority to improve PEC water splitting. Up to now, various photoelectrodes have been developed in photocatalysis, such as In₂O₃ [3], TiO₂ [4], WO₃, [5] BiVO₄, [6] α -Fe₂O₃ [7]. In particular, In₂O₃ with the low toxicity and stable physicochemicali could be considered as an ideal candidate material, and it has received extensive attention in photo-splitting of water [8]. However, it remains a huge challenge to further improve the performance of In₂O₃ because of the present of the ultrafast charge carrier recombination, deeply active holes trapping in trap state (TS) and narrow light response range. Therefore, much effort has been implemented to improve PEC performance of In₂O₃, such as ion doping, construction of heterojunction, oxygen vacancy [9–12]. To significantly improve the charge separation efficiency, considerable attempts have been adopted to develop In₂O₃-based heterostructures, such as CuO/In₂O₃, [13] In₂O₃/TiO₂, [14] In₂O₃/In₂S₃ [15]. In particular, the Z-scheme heterojunction is found to be an effective strategy to achieve efficient charge separation in photocatalysis [16,17]. This Z-scheme system could not only optimize redox potential, but also promote the charge separation driven by the interfacial electric field [18,19], such as $Fe_2O_3/g-C_3N_4$, [20] $Bi_2WO_6/GQDs/WO_3$, [21] CuInS/g- C_3N_4 [22]. However, up to date, it's still a big challenge to construct In₂O₃-based catalysts for full-spectrum photocatalysis. Therefore, selecting suitable semiconductor to combine with In₂O₃ for constructing heterojunction with Z-scheme transfer mechanism is a promising strategy to enhance light absorption and improve the PEC performance.

With the matched band structure and Fermi level of In₂O₃, the hematite (α -Fe₂O₃) could be served as an ideal candidate due to its suitable energy band structure, topping stability in an alkaline solution, and superior theoretical solar-to-hydrogen efficiency of 15.8 % [23–27]. The photo-induced electrons on In₂O₃ with lower conduction band potential will combine with the holes on α -Fe₂O₃ with higher valence band potential, while the electrons and holes with stronger redox ability remain on α -Fe₂O₃ and In₂O₃, respectively. However, there are still no reports about the construction of direct Z-scheme Fe₂O₃/In₂O₃ heterojunction.

In this work, we construct the Ti-Fe₂O₃/In₂O₃ Z-scheme photoanode

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Fig. 1. Schematic illustration for the fabrication of Ti-Fe₂O₃/In₂O₃ nanoarrays.

with reasonable energy band structure to acquire in-depth understanding on the relationship between the charge transfer behavior at the builtin electric field and PEC performance. As a result, the optimized 150Ti-Fe₂O₃/In₂O₃ shows higher PEC activities with the photocurrent density as high as 2 mA/cm² at 1.23 V vs. RHE, which is 7 times higher than pure In₂O₃. The adjustable interfacial electric field enable Ti-Fe₂O₃/In₂O₃ as an efficient photoanode for water splitting. And the effective interfacial Z-scheme charges transfer behavior could be fully proved by TAS measurement, and in-situ double-beam detection strategy (AM 1.5 + 405 nm). Accordingly, the high PEC performance of Z-scheme Ti-Fe₂O₃/ In₂O₃ photoanode for the oxygen evolution reaction could be attributed to the enhancing separation and transportation of charge carriers driven by the built-in electric field.

2. Result and discussion

2.1. Preparation of photoanode

Synthesis of Ti-Fe₂O₃: The Ti-Fe₂O₃ nanorods array were synthesized on FTO through a hydrothermal method reported previously [25]. It should be noted that the FTO glass was sonicated 20 min in deionized water, ethanol, acetone, ethylacetate and ethanol successively before placing it in the Teflon-lined autoclave. The precursor solution has been prepared by dissolving 0.15 M iron chloride hexahydrate (FeCl₃·6H₂O), 1 M sodium nitrate (NaNO₃). Here, the 1 % titanium tetrachloride (TiCl₄) ethanol solution (volume percentage) was added to the precursor solution with different doping volume (100 μ L, 150 μ L, and 200 μ L). Then, the FTO with its conductive side facing the Teflon-lined autoclave down was immersed in the above solution. Subsequently, the autoclave was transferred to an oven for 12 h, which was preadjusted to 100 °C. The synthesized Ti-Fe₂O₃ was annealed at 550 °C for two hours under air atmosphere.

Synthesis of Ti-Fe₂O₃/In₂O₃: The In₂O₃ cubes were synthesized on Ti-Fe₂O₃ through a hydrothermal method reported previously [28]. The precursor solution has been prepared by dissolving 0.5725 g In₂O₃.4.5H₂O and 0.18 g urea. Then the Ti-Fe₂O₃ with its conductive side facing the Teflon-lined autoclave down was immersed in the above solution after stirring for 30 min. Finally, the synthesized Ti-Fe₂O₃/In₂O₃ was annealed at 400 °C for two hours under air atmosphere. It is noted that the hydrothermal reaction was carried out for 2 h, 6 h and 10 h at 160 °C to obtain Ti-Fe₂O₃/2h-In₂O₃, Ti-Fe₂O₃/6h-In₂O₃

and Ti-Fe₂O₃/10h-In₂O₃ when the doping volume of Ti⁴⁺ was 150 μ L, respectively. Then 100Ti-Fe₂O₃/In₂O₃, 150Ti-Fe₂O₃/In₂O₃, and 200Ti-Fe₂O₃/In₂O₃ were obtained according to the different doping volume of Ti⁴⁺ under keeping the reaction time of In₂O₃ constant (6 h), respectively. The preparation procedure was shown in Fig. 1.

2.2. Characterizations

The crystal structure and the phases of the photoanodes were analyzed using X-ray diffraction (XRD, D/MAX2250 diffractometer) in the range from 10° to 80° at a scan rate of 10° /min. The surface morphology and film thickness were characterized using field-emission scanning electron microscopy (SEM; Hitachi Company) and highresolution transmission electron microscopy (HR-TEM; FEI Tecnai G2 F20). The surface chemical state of elements was evaluated by X-ray photoelectron spectroscopy (XPS) using the C 1s peak as a correction. The UV–vis absorption spectrum of the samples was obtained for the range of 300–800 nm by an UV–vis-NIR spectrophotometer (Shimadzu UV-3600). The separation and kinetic behaviors of photogenerated charge carriers were studied with the aid of lock-in-based SPV measurement on a home-made equipment. The WF measurement was carried out on the Kelvin probe instrument (SKP 5050, KP Technology Ltd, UK).

The transient absorption spectroscopy (TAS) was measured with an amplified Ti: sapphire femtosecond laser (800 nm wavelength, 50 fs, 1 kHz repetition; Coherent Libra) and a Helios pump/probe setup (Ultrafast Systems LLC). The pump beam of 400 nm fs laser was obtained by frequency doubling the 800 nm fundamental regenerative amplifier output with a BBO crystal. In addition, the white-light probe continuum was generated by focusing the fundamental 800 nm beam from Ti: sapphire laser onto a sapphire plate (2 mm thick), and the probe beam was focused (50 μ m in diameter) at the center of the pump beam (2 mm in diameter) on the sample.

2.3. PEC measurements

All PEC measurements were explored under A 300 W xenon lamp (Micro solar 300, Beijing Perfect light) simulated AM 1.5 G illumination (100 mW/cm²) from the photoanode side with an electrochemical station (CHI 660E) in a standard three-electrode configuration, which consisting of the prepared photoanodes, Pt, and Ag/AgCl as the working



Fig. 2. Top-view SEM images of (a) In_2O_3 , (b) 150Ti-Fe₂O₃/ In_2O_3 . (c) The corresponding cross section images of 150Ti-Fe₂O₃/ In_2O_3 film. (d) HR-TEM image of 150Ti-Fe₂O₃/ In_2O_3 . (e) EDS elemental mapping of Fe, O, In, Ti of 150Ti-Fe₂O₃/ In_2O_3 .

electrode, counter electrode, and reference electrode, respectively. The applied potential versus Ag/AgCl was translated into potential versus RHE based on the Nernst equation:

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl}^{\theta}$$

The electrolyte in our PEC measurements was 1 M KOH (pH = 13.8) unless otherwise specified, and the active area was 0.283 cm². The current vs potential curve was obtained by linear sweep voltammetry (LSV) at a scan rate of 10 mV/s. Applied bias photon to current efficiency (ABPE) was calculated via the following equation:

$$ABPE = \left(J_{light} - J_{dark}\right) imes \left(rac{1.23 - V_{RHE}}{P_{light}}
ight)$$

While J_{light} and J_{light} referred to the current densities of the synthesized photoanodes under illumination and in dark, respectively. V_{RHE} referred to the applied potential versus RHE, and P_{light} referred to the incident light intensity (100 mW/cm²). The accumulated charge densities of the Ti-Fe₂O₃/In₂O₃ film were obtained by integrating the transient photocurrent density at different potential values from 0.8 to 1.6 V_{RHE}. The injection efficiency of the photoanodes were obtained through employing 0.5 M H₂O₂ as a hole scavenger in 1 M KOH electrolyte, the oxidation of H₂O₂ is thermodynamically and kinetically more favorable than water. The injection efficiency (η_{inj}) was determined by using following equation:

$$\eta_{\rm ini} = J_{\rm H_2O}/J_{\rm H_2O_2}$$

While J_{H_2O} , $J_{H_2O_2}$ referred to the photocurrent density for PEC H₂O oxidation and PEC H₂O₂ oxidation, respectively. In the presence of hole scavenger H₂O₂, the surface recombination of charge carriers can be

completely suppressed without influencing the charge separation in the electrode bulk (i.e., $\eta_{inj}=100$ %). Thus, the charge separation could be calculated as following equation:

$$\eta_{sep} = J_{H_2O_2}/J_{abs}$$

The separation efficiency of photogenerated charge carriers during reaction was characterized by the difference values of open circuit potential between dark and illumination. The EIS was measured with a frequency range of 10^5 Hz to 0.05 Hz at 1.0 V vs. RHE under illumination (100 mW/cm²) to ascertain the charge transport of the photoanode. In addition, Incident photon to current conversion efficiency (IPCE) was carried out at 1.23 V vs. RHE with the help of a monochromator, and the intensity of monochromatic light was measured by a calibrated Si photodiode. IPCE was obtained according to the equation:

$$IPCE = \frac{J \times 1240}{P_{mono} \times \lambda}$$

The Mott-Schottky analysis: in the M–S plot, the flat band potential of the photoelectrode is measured according to following equation

$$\frac{1}{C^2} = \frac{2}{e\varepsilon\varepsilon_0 N_D} \left[(E - E_{FB}) - \frac{T}{e} \right]$$

in which C is the space charge capacitance, e is the electron charge, \sum is the vacuum permittivity (8.85 × 10⁻¹² F m⁻¹), \sum 0 is the relative dielectric constant of hematite (\sum 0 = 80), ND is the charge donor density (cm⁻³), E is the electrode applied potential, EFB is the flat band potential, | is the Boltzmann's constant (1.38 × 10⁻²³ J K⁻¹) and T is the absolute temperature (in K).



Fig. 3. (a) Current density-potential curves of pure Ti-Fe_2O_3 , \ln_2O_3 and $\text{Ti-Fe}_2O_3/\ln_2O_3$. (b) LSV curves under chopped light. (c) IPCE plots of pure Ti-Fe_2O_3 , \ln_2O_3 and $\text{Ti-Fe}_2O_3/\ln_2O_3$ at 1.23 V vs. RHE. (d) The PEC OER stability test of 150Ti-Fe}_2O_3/\ln_2O_3 photoanode at 1.23 V vs. RHE in KOH and KOH + Urea electrolyte. (e) Injection efficiency of pure Ti-Fe}_2O_3 and Ti-Fe}_2O_3/In_2O_3 photoanode. (f) The bulk charge separation efficiency of pure Ti-Fe}_2O_3/In_2O_3 in KOH+H_2O_2 electrolyte.

3. Result and discussion

3.1. Composition and chemical states

XRD was conducted to determine the crystal structure of the obtained photoanode. The XRD patterns of the representative pure In_2O_3 , and all XRD diffraction peaks (30.5°, 35.5°, 37.9°, and 51.5°) are well matched with the standard card of In_2O_3 (PDF#06-0416) (Fig. S1a) [3. 29]. In addition, it is evident that all diffraction peaks of $Ti-Fe_2O_3/In_2O_3$ could be indexed to In_2O_3 and $Ti-Fe_2O_3$ (PDF#33-0664) [30] after introducing Ti-Fe₂O₃ (Fig. S1b), which indicate that the successful synthesis of composite photoanode. The morphological evolution of the Ti-Fe₂O₃/In₂O₃ (2 h, 10 h) are displayed by SEM. With increasing hydrothermal-time from 2 to 10 h, the growing number of 3D cubic were observed in Ti-Fe₂O₃ arrays (Fig. S2). At the same time, the pristine In₂O₃ (6 h) exhibits cubic structure with a diameter of approximately 80 nm (Fig. 2a), and the In₂O₃ on the surface of 150Ti-Fe₂O₃/In₂O₃ has no evident changes compared with the pure In₂O₃ (Fig. 2b). Further, the cross-section confirms that In₂O₃ wrap around the Ti-Fe₂O₃ nanorods (Fig. 2c). To determine the crystalline structure of 150Ti-Fe₂O₃/In₂O₃ heterojunction, the lattice spacings of 0.367 nm from the HR-TEM (Fig. 2d), which is indexed to (102) planar of Ti-Fe₂O₃ [31]. Another interplanar spacing of 0.282 nm obtained from the inner nanorods belongs to the (222) plane of In₂O₃ [32]. The results of the HR-TEM demonstrate the 150Ti-Fe $_2O_3/In_2O_3$ heterojunction photoanode have been successfully synthesized. Furthermore, Energy-dispersive X-ray spectroscopy (EDS) elemental mapping illustrates the existence and uniform distribution of Fe, O, In and Ti element in 150Ti-Fe₂O₃/In₂O₃ (Fig. 2e). Besides, the X-ray photoelectron spectroscopy (XPS) analysis could be used to further determine the valence and chemical composition of Ti-Fe₂O₃/In₂O₃. Notably, the O 1s state can be indexed to the lattice oxygen and hydroxyl oxygen in Ti-Fe₂O₃/In₂O₃ composites (Fig. S3a). And the survey spectrum demonstrates the coexistence of Fe, O, In and Ti elements (Fig. S3b).

3.2. PEC performance

The PEC performance of all In2O3-based photoanodes was systematically investigated by LSV curves under solar simulated illumination in 1 M KOH aqueous solution [33,34]. LSV curves of different arrays are tuned by regulating the Ti doping volume under a reaction time of 6 h as shown in Fig. 3a. For the convenience of description, the samples could be denoted as 100Ti-Fe₂O₃/In₂O₃ (100 µL), 150Ti-Fe₂O₃/In₂O₃ (150 µL) and 200Ti-Fe₂O₃/In₂O₃ (200 µL). Especially, the 150Ti-Fe₂O₃/In₂O₃ photoanode already exhibits a remarkable photocurrent density of 2.0 mA/cm^2 at 1.23 V vs. RHE as shown in Fig. S4a, which is 7 and 5 times higher than In₂O₃ and pure Ti-Fe₂O₃, respectively. The transient photocurrent responses under chopped light shown in Fig. 3b, it demonstrated that efficiently extract photogenerated holes from bulk Ti-Fe₂O₃ and thus ending up with separation of photogenerated electron-hole pairs for water oxidation. More importantly, the IPCE spectra as a function of wavelength are measured to verify the effect of monochromatic light upon the photocurrent density. As shown in Fig. 3c, the IPCE spectra of Ti-Fe₂O₃/In₂O₃ is much higher than that of pristine In₂O₃ and Ti-Fe₂O₃ within the specific wavelength range (390–570 nm), and the highest IPCE value achieves 70 % (100Fe₂O₃/In₂O₃), 82 % (150Ti-Fe₂O₃/In₂O₃), 52 % (200Ti-Fe₂O₃/In₂O₃), 20 % (Ti-Fe₂O₃) and 26 % (In₂O₃) at 390 nm, respectively. As shown in Fig. S4b, we can infer that the interfacial electric field between $\mathrm{Ti}\text{-}\mathrm{Fe_2O_3}$ and $\mathrm{In_2O_3}$ could play a major role to improve the charge transfer performance (390-410 nm). More importantly, the 150Ti-Fe₂O₃/In₂O₃ can maintain about 96 % of the initial photocurrent density after 2 h photostability measurement shown in Fig. 3d, which indicate its photostability in PEC water splitting reaction and oxidized urea [35]. In addition, the injection efficiencies of Ti-Fe₂O₃/In₂O₃ in 1 M KOH in Fig. 3e. Herein, 150Ti-Fe₂O₃/In₂O₃ heterojunction photoanode shows the highest injection efficiency than those of photoanode. And the bulk charge separation efficiency is calculated for PEC water oxidation in the electrolyte with a sacrificial donor of H₂O₂ in Fig. 3f. This result illustrates that the Z-scheme 150Ti-Fe₂O₃/In₂O₃ heterojunction is favorable to alleviate the severe



Fig. 4. (a) Opencircuit potentials (OCP) of pure Ti-Fe₂O₃, In₂O₃ and Ti-Fe₂O₃/In₂O₃ electrodes measured in the dark (red) and under illumination (black) in 1 M KOH electrolyte. (b) Nyquist plots of pure Ti-Fe₂O₃, In₂O₃ and Ti-Fe₂O₃/In₂O₃ photoanode at 1.1 V vs. RHE under AM 1.5 G illumination. (c) Nyquist plots of 150Ti-Fe₂O₃/In₂O₃ photoanode at 1.1 V vs. RHE under AM 1.5 G + 405 nm illumination. (d) SPV signal of In₂O₃ and Ti-Fe₂O₃/In₂O₃ photoanode. The inset shows the schematic of SPV measurements (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

bulk recombination and sluggish surface reaction for Fe₂O₃. To optimize the hydrothermal time under the certain 150 μ L Ti doping concentration, it is harmful to optimize PEC activity of In₂O₃-based arrays at the short (2 h) or long (10 h) hydrothermal time in Fig. S5a, It shows that the highest photocurrent density at 1.23 vs. RHE of Ti-Fe₂O₃/In₂O₃ has achieved at a hydrothermal time of 6 h. And this catalytic for the urea oxidation reaction also possess outstanding ability in Fig. S5b. The ABPE and injection efficiency of Ti-Fe₂O₃/6h-In₂O₃ also confirm that the photoanode has the best PEC performance as shown in Fig. S5c-d.

As we know, three factors, including the light absorption, the injection effeciency and the separation efficiency, could be taken into account for the improvment of PEC performance [36]. In order to further understand the effect of the light absorption on PEC water oxidation reaction, we investigate the UV-vis DRS. As shown in Fig. S6a, When Ti-Fe₂O₃ nanorods are embedded into In₂O₃ to form the Ti-Fe₂O₃/In₂O₃ heterojunction, the visible light absorption edge increases significantly (from 400 to 600 nm). And the light absorption edge of Ti-Fe₂O₃ and Ti-Fe₂O₃/In₂O₃ photoanodes are all recorded in the wavelength of around 600 nm. Therefore, the light absorption of In₂O₃ is expanded after constructing a Ti-Fe₂O₃/In₂O₃ heterojunction. Based on the Tauc plot in Fig. S6b, there is no obvious distinction between Ti-Fe₂O₃/In₂O₃ and the pure Ti-Fe₂O₃ in light absorption edge. Therefore, combining with the result of injection efficiencies and bulk charge separation efficiency, it is reasonable to deduce that the improvement of PEC performance can be ascribed to the the enhancing efficient charge separation and migration.

The open-circuit photovoltage (OCP) as a function of separation efficiency of photo-generated charges is carried out. As shown in Fig. 4a, the samples of Ti-Fe₂O₃/In₂O₃ have the higherOCP values in comparison with In₂O₃. Especially, the 150Ti-Fe₂O₃/In₂O₃ has the highest OCP values (Δ OCP = OCP_{dark} –OCP_{light}), which indicates that enhanced charge separation when the optimized built-in electric field formed in the 150Ti-Fe₂O₃/In₂O₃ heterojunction. To gain additional insights about the charge transfer, the Mott-Schottky (M–S) plots were obtained with a frequency of 1000 Hz. As shown in Fig. S7a, the M–S plot of 150Ti-Fe₂O₃/In₂O₃ shows a much flatter slope than that of other

photoanodes, and the charge carrier densities (N_D) of the photoanodes can be calculated by adopting the slopes of the M–S plots in Fig. S7b-f, which are 4×10^{19} cm⁻³, 1.54×10^{20} cm⁻³, 5×10^{19} cm⁻³, 4.7×10^{19} cm⁻³, and 3.1×10^{19} cm⁻³ for pure Ti-Fe₂O₃, 150Ti-Fe₂O₃/In₂O₃, 100Ti-Fe₂O₃/In₂O₃, 200Ti-Fe₂O₃/In₂O₃ and In₂O₃, respectively. These results suggest that the higher donor density of 150Ti-Fe₂O₃/In₂O₃ results in lower resistance and faster charge transfer rate, which favoring the photocatalytic water splitting. In addition, the typical electrochemical impedance spectroscopy (EIS) analysis is evaluated the charge transfer at the interface. It should be noted that the semicircles at high frequency region represent charge transfer in the bulk photoanode and the semicircles at low frequency region are related to charge transfer process at the photoanode/electrolyte interface [37]. As show in Fig. 4b, compared with the pure Ti-Fe₂O₃, the smaller radius of the Ti-Fe₂O₃/In₂O₃ composite photoanode could be contributed to the synergy of interfacial electric field between Ti-Fe₂O₃ and In₂O₃ and the changing morphology in surface. However, compared with 100Ti-Fe2O3/In2O3 and 200Ti-Fe2O3/In2O3 composite photoanode, 150Ti-Fe₂O₃/In₂O₃ shows the smallest radius, which could be only contributed to the role of the interfacial electric field, because the same In2O3 is loaded on the surface. Nyquist plots are fitted by equivalent circuit, as shown in Fig. S9, and the fitted values are listed in Table S1. The 150Ti-Fe₂O₃/In₂O₃ photoanode yields a smallest R_1 value (116.3 Ω) compared to 100Ti-Fe₂O₃/In₂O₃ (140.9 Ω), 200Ti-Fe₂O₃/In₂O₃ (148.9 Ω), and pure Ti-Fe₂O₃ (461.9 Ω), which demonstrates the decreasing interfacial charge resistance at the interface between the In₂O₃ and the Ti-Fe₂O₃. To further enlarge the role of interfacial charge transfer, another 405 nm light is used to excite Ti-Fe₂O₃ at the same time in Fig. 4c, which indicates that the enhanced interfacial charge transfer could achieve effective charge separation of Ti-Fe₂O₃/In₂O₃ heterostructure (The sample is denoted as150Ti-Fe₂O₃/In₂O₃-D). Therefore, we infer that the effective charge separation of 150Ti-Fe₂O₃/In₂O₃ heterojunction photoanode is possibly ascribed to the role of interfacial electric filed.

To thoroughly clarify the interfacial electric filed between $Ti-Fe_2O_3$ and In_2O_3 could provide the driving force for accelerating



Fig. 5. (a) WF mapping measurements of Ti-Fe₂O₃ (100 µL, 150 µL, 200 µL) and In₂O₃. (b) The diagram of Ti-Fe₂O₃/In₂O₃ charge transfer under the role of interface electric field.

photogenerated charge separation and promote the migration of charge carriers, the SPV measurement (Introduction of instruments in supporting information) is explored to investigate the behavior of photogenerated charges at the Ti-Fe₂O₃/In₂O₃ interface [38–40]. The positive signal represents that the holes transfer to the surface while negative signal indicates that the migration of electrons to the surface. Herein, the SPV spectra of Ti-Fe₂O₃/In₂O₃ heterojunction with front side illumination (the monochromatic light illuminated from the In₂O₃ side) are investigated as shown in Fig. 4d. Gratifyingly, the 150Ti-Fe₂O₃/In₂O₃ photoanode has the stronger positive signal than In₂O₃ under the action of interfacial electric field, meaning the higher separation efficiency compared with pure In₂O₃.

3.3. Z-scheme charge transfer mechanism of Ti-Fe₂O₃/In₂O₃

According to the above results, the internal built-in electric field directed from In_2O_3 to Ti-Fe₂O₃ at the interface is formed, which benefits the separation and transfer of photogenerated carriers via the Z-scheme pathway [41,42]. Therefore, the relationship between the interface built-in electric field and Z-scheme charge transfer mechanism is necessary to further research. Generally, the charge transfer between two semiconductors depends on the interface band bending, which is further determined by their Fermi levels [43].Inspired by this research, we investigate the driving force at the interface electric field through the WF measurement, which directly reveals the contact potential difference (CPD) between the samples and the Au probe. The WF values of In_2O_3 and Ti-Fe₂O₃ are calculated according to the following equation 1:

$$\Phi_{\text{sample}} = \Phi_{Au} + eCPD(\Phi_{Au} = 4.8 \ eV)$$

Here, the different volume of Ti^{4+} of Ti-Fe₂O₃ could lead to different Fermi level. As the Ti^{4+} doping volume increases from 100 µL to 200 µL, the Fermi level of Ti-Fe₂O₃ gradually near the vacuum level [44,45]. In Fig. 5a, the WF values of 100Ti-Fe₂O₃, 150Ti-Fe₂O₃, 200Ti-Fe₂O₃ and In₂O₃ are 4.875 eV, 4.862 eV, 4.860 eV and 5.052 eV, respectively. Therefore, when Ti-Fe₂O₃ and In₂O₃ contact directly, Ti-Fe₂O₃ could form an upward bend and In_2O_3 could formed a downward bend. It is beneficial for the electrons to transfer from In_2O_3 to Ti-Fe₂O₃, which indicating that the charge between Ti-Fe₂O₃ and In_2O_3 will mainly transport by the Z-scheme mechanism. In addition, the Δ WF value (Δ $WF = WF_{In} - WF_{Fe}$) as shown in Table S2, the large Δ WF value leads to the intensive interfacial electric field. Therefore, we infer the direction of charge migration as shown in Fig. 5b. Conversely, a traditional type II charge-transfer pathway requires more energy due to band bending and internal electric field. Therefore, more electrons on In_2O_3 are in inclined to accumulating at the interface followed by the Z-scheme mechanism. However, the doped Ti in excess (200 µL) can provide recombination centers by creating inter-bandgap energy states.

To further monitor the electron-hole separation and elucidate the efficient interfacial charge transfer of Ti-Fe₂O₃/In₂O₃ via a direct Zscheme pathway, time-resolved transient absorption spectra (TAS) of samples were performed under 400 nm excitation to track the real-time photogenerated carrier dynamics [46,47]. As illustrated in Fig. 6a-d, the broad negative absorption band were observed for both Ti-Fe₂O₃, 100Ti-Fe₂O₃/In₂O₃, 150Ti-Fe₂O₃/In₂O₃ and 200Ti-Fe₂O₃/In₂O₃, mainly due to stimulated emission and the state filling of photobleaching [48]. It is consistent with the two absorption band edges of Ti-Fe₂O₃ in UV-vis absorption spectra (470 cm^{-1} and 580 cm^{-1}). After combing with In₂O₃, the present of positive signal could be contributed to the holes of Ti-Fe₂O₃ combine with the electrons of In₂O₃ at the interfere. Typically, 150Ti-Fe₂O₃/In₂O₃ shows the lowest negative signal and highest positive signal as compared to other Ti-Fe₂O₃/In₂O₃. Moreover, the weakened negative signal and the increasing positive signal indicate that the number of holes on Ti-Fe2O3 is reduced, which proves that more holes of Ti-Fe₂O₃ combine with the electrons of In₂O₃ at the interface. To estimate the decay kinetics of photo-generated holes, the time profiles of the TAS probed at 585 nm were fitted by a two-exponential function in Fig. 6e-i, and the corresponding exponential fitted parameters are listed in Table S3. Generally, the short lifetime (τ_1) and long lifetime (τ_2) components result from holes trapped at shallow and deep sites before their recombination [49]. Compared to pure Ti-Fe₂O₃ (τ_1 : 0.79 \pm 0.008 ps; $\tau_2\!\!:$ 20.43 \pm 0.40 ps), the decay lifetimes of 150Ti-Fe_2O_3/In_2O_3

Y. Li et al.



Fig. 6. TAS measurements: a) Ti-Fe₂O₃, b) 100Ti-Fe₂O₃/In₂O₃, and c) 150Ti-Fe₂O₃/In₂O₃, d) 200Ti-Fe₂O₃/In₂O₃ after irradiation with a 400 nm laser flash, (e) Time profiles of normalized TAS at 580 nm. Experimental decay kinetics fitted under 580 nm: f) Ti-Fe₂O₃, g) 100Ti-Fe₂O₃/In₂O₃, h) 150Ti-Fe₂O₃/In₂O₃, i) 200Ti-Fe₂O₃/In₂O₃, of a construction of the second seco

photoanode are largely decreased to $(0.64 \pm 0.015 \text{ ps})$ and $(8.96 \pm 0.32 \text{ ps})$. Meantime, the pseudocolor TA plots of Ti-Fe₂O₃/In₂O₃ under 400 nm fs excitation with ~0.8 mJ fluence at 1 kHz repetition rate shown in Fig. 7 a–d. These results fully indicate that the effective charge transfer at interfacial electric field follow the Z-scheme mechanism.

To acquire in-depth exploring the Z-scheme migration mechanism of Ti-Fe₂O₃/In₂O₃ photoanodes, an in-situ double-beam detection strategy based on PEC measurement is carried out [50,51]. In our design, we adopted a Xenon light source (AM 1.5) to illuminate the In₂O₃ side of the Ti-Fe₂O₃/In₂O₃/CoPi when the CoPi layer is loaded to further optimize photoanode performance. Meantime, another light source (405 nm) is uesd to illuminate the Ti-Fe₂O₃ side in Fig. S9. Here, the interfacial electric field could be enhanced under double beams illumination (denoted as Ti-Fe₂O₃/In₂O₃/CoPi-D), when we only use 405 nm light or AM 1.5 to illuminate Ti-Fe₂O₃/In₂O₃/CoPi, the photocurrent is 3.8 mA/cm² and 2.8 mA/cm² at 1.23 V versus RHE, respectively. As expected, the current could reach 6.8 mA/cm² at 1.23 V versus RHE when we use double beams to illuminate Ti-Fe₂O₃/In₂O₃/CoPi, which is much higher than each single light illumination. The enhancing photocurrent is due to that the enhanced interface electric field strengthens the potential barrier, leading that more electrons of In₂O₃ recombine with the holes of the Ti-Fe₂O₃ at internal electric field, and more holes migrate to the surface of In₂O₃ to participate in the water splitting. This result is consistent with the performance of the Z-scheme migration mechanism.

migration pathway for a direct Z-scheme Ti-Fe₂O₃/In₂O₃ system. A positive shift in the binding energy indicates a decreasing of the electron density, whereas a negative shift indicates an increasing of the electron density. Therefore, the shift of binding energy in the XPS spectra can be utilized for determining the electron-migration pathway for a direct heterojunction with Z-scheme transfer mechanism [42,52,53]. As shown in Fig. 8a, the In 3d state of the 100Ti-Fe₂O₃/In₂O₃ and 150Ti-Fe₂O₃/In₂O₃ composites is found to shift toward the higher-energy region compared with pure In₂O₃. Meanwhile, the Ti 3p states of the 100Ti-Fe₂O₃/In₂O₃ and 150Ti-Fe₂O₃/In₂O₃ in Fig. 8b. These results further confirm that the direct Z-scheme charge transfer mechanism between the In₂O₃ and the Ti-Fe₂O₃.

According to the above analysis, the Ti-Fe₂O₃/In₂O₃ Z-scheme process could be deduced, and the schematic band diagram of Ti-Fe₂O₃/In₂O₃ based on Z-scheme charge-transfer mechanism is illustrated in Scheme 1. Briefly, when In₂O₃ and Ti-Fe₂O₃ contact to form the Z-scheme heterojunction, the Ti-Fe₂O₃ could form an upward bend, whereas In₂O₃ could form a downward bend. Hence, the electrons on In₂O₃ with lower conduction band potential will combine with the holes on Ti-Fe₂O₃ with higher valence band potential, which could promote the charge separation of In₂O₃ in the bulk. And meanwhile, more holes migrate to the surface of In₂O₃ to participate in the oxidation reaction of water.

XPS spectra could also be utilized for further confirming the electron-



Fig. 7. Pseudocolor TA plots of Ti-Fe₂O₃/In₂O₃ under 400 nm fs laser pulses with ~0.8 mJ fluence at 1 kHz repetition rate.



Fig. 8. (a) XPS with peak for In 3d deconvolutions for Ti-Fe₂O₃/In₂O₃ and In₂O₃. (b) XPS with peak for Ti 3p deconvolutions for Ti-Fe₂O₃/In₂O₃ and In₂O₃.

4. Conclusion

In summary, the Z-scheme Ti-Fe₂O₃/In₂O₃ photoanode has provided an archetype to exploit the effective charge separation by adjusting the interfacial electric field. Impressively, the optimized 150Ti-Fe₂O₃/In₂O₃ photoanode shows a high photocurrent density of 2 mA/cm² at 1.23 V vs. RHE, which is nearly 7 times higher than the pure In₂O₃. The results of TAS and SPV measurement confirm that the Ti-Fe₂O₃/In₂O₃ composite exhibits the effective electron transfer from In₂O₃ to Ti-Fe₂O₃ and the outstanding long-lived charge separation performance due to the established interfacial electric field. This work provides deeper insight into the charge carriers' behavior on the direct Z-scheme photoanode and exhibit the effect of interfacial electric field for the enhancement of water splitting.

CRediT authorship contribution statement

Yinyin Li: Conceptualization, Methodology, Validation, Investigation, Writing - original draft, Visualization. Qiannan Wu: Methodology, Investigation. Yifan Chen: Investigation. Rui Zhang: Investigation, Formal analysis. Cuiyan Li: Formal analysis, Software. Kai Zhang: Validation, Formal analysis, Visualization. Mingjie Li: Writing - review & editing. Yanhong Lin: Writing - review & editing. Dejun Wang: Writing - review & editing. Xiaoxin Zou: Writing - review & editing. Tengfeng Xie: Conceptualization, Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare no conflict of interest.



Scheme 1. Schematic band diagram of Ti-Fe₂O₃/In₂O₃.

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Appendix A. Supplementary data

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