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Promoting Photoelectrochemical Water Oxidation on Ti-Doped Fe₂O₃ Nanowires Photoanode by O₂ Plasma Treatment

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Abstract: Surface electron traps on semiconductor photoanodes mediate surface recombination and deteriorate the photoelectrochemical (PEC) water oxidation performance of the photoanode. Developing convenient methods to reduce surface electron traps is therefore essential for high efficiency PEC water oxidation on semiconductor photoanodes, particularly for nanostructured photoanodes with large surface area. Herein, we employ a O₂ plasma treatment to boost the PEC water oxidation performance of Ti-doped Fe₂O₃ (Ti-Fe₂O₃) nanowires photoanodes, aiming to reduce surface oxygen vacancies, the dominant electron traps on Ti-Fe₂O₃ surface. X-ray diffraction (XRD), scanning electron microscopy and spectroscopic analyses show that the oxygen plasma treatment changes the structural, morphological and optical properties negligibly, but it does reduce the content of surface oxygen vacancies, as estimated from O1s X-ray photoelectron spectroscopy spectra. An optimal O₂ plasma treatment (200 W, 70 s) increases the photocurrent density of the Ti-Fe₂O₃ nanowire photoanode to 2.14 mA·cm⁻² (1.23 V vs. RHE) under air mass 1.5G simulated solar light, which is 1.95 times higher than the pristine Ti-Fe₂O₃ nanowire photoanode. The surface hole transfer efficiency is also improved by 1.66 times due to the reduced surface recombination. The work suggests that O₂ plasma treatment is a convenient but effective method to boost the PEC water oxidation performance of Ti-Fe₂O₃ photoanode and might be applicable to other semiconducting oxide photoanodes for high efficiency PEC water splitting.

Keywords: photoelectrochemical water splitting; O₂ plasma treatment; surface oxygen vacancies; Ti-doped hematite nanowire arrays



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1. Introduction

Photoelectrochemical (PEC) water splitting into hydrogen and oxygen with a semiconductor photoanode is regarded as a promising strategy to provide clean and sustainable energy since it was first reported by Fujishima and Honda in 1972 [1], in which a highly efficient photoanode plays a decisive role. The nanostructured Fe₂O₃ photoanode has attracted a large number of investigations due to its suitable photon absorption (2.0–2.2 eV), shortened minority diffusion distance, and large contact area with the electrolyte for surface reactions [2–5]. However, the large surface area of nanostructural Fe₂O₃ usually introduces many surface states, such as surface oxygen vacancies and Fe²⁺ sites, which mediate the unwanted surface charge recombination [6–9]. Thus, it is an essential issue to reduce the surface states of the Fe₂O₃ photoanode for high efficiency PEC water splitting.

Surface modification of the passivation layer and loading of the cocatalyst are usually adopted to reduce the surface recombination mediated by surface oxygen vacancies and improve the PEC performance of Fe₂O₃ photoanodes [10–14]. For example, Zou et al. demonstrated that the ion-impermeable Al₂O₃ layer on Ti-Fe₂O₃ nanorods passivated the surface states and suppressed the back reaction, which improved the photocurrent onset

potential [14]. The result proved the necessity of surface states treatment of Ti-doped Fe_2O_3 nanowire photoanodes. However, the methods of surface loading the passivation layer and cocatalyst have some drawbacks, introducing a barrier in the interface or reducing the absorption of photons. In addition, Yu et al. reported that the most significant issue in suppressing the surface states of Fe_2O_3 was to reduce the oxygen vacancies on the surface of the electrode [15]. Therefore, it is still necessary to develop a convenient and effective method to controllably tune the surface oxygen vacancy states of Fe_2O_3 photoanodes.

Herein, we employed oxygen plasma treatment to reduce the surface oxygen vacancy of Ti-doped Fe_2O_3 (Ti- Fe_2O_3) nanowire photoanodes. Oxygen plasma, consisting of highly reactive oxygen ions with large concentration and kinetic energy, is expected to oxidize the surface of Ti- Fe_2O_3 in a convenient way without introducing impurities. The effect of oxygen plasma on the surface states and PEC performance of Ti- Fe_2O_3 photoanodes were investigated. At an optimal treatment condition (200 W, 70 s), the PEC performance of Ti- Fe_2O_3 photoanodes was remarkably improved, exhibiting a 1.95 times higher photocurrent than the pristine Ti- Fe_2O_3 photoanode at the potential of 1.23 V vs. reversible hydrogen electrode (RHE). The surface hole transfer efficiency of the plasma-treated Ti- Fe_2O_3 (OPT-Ti- Fe_2O_3) photoanode reached 78%, 1.66-fold higher than the pristine one. O1s X-ray photoelectron spectroscopy (XPS) analysis showed that the integrated area ratio of oxygen vacancy to lattice oxygen at the surface of the OPT-200W-70s electrode was reduced by 6.7%. The work suggests that O_2 plasma treatment is a convenient but effective method for tuning the surface defect states of semiconducting oxides photoanode for enhanced PEC water splitting.

2. Results and Discussion

2.1. Effect of O_2 Plasma on Morphology, Structure, and Optical Properties of the Electrodes

Ti- Fe_2O_3 nanowire photoanodes were selected to investigate the effect of O_2 plasma treatment on the PEC water oxidation performance. The films were synthesized on F-doped SnO_2 conductive glass (FTO) substrates via a hydrothermal method and post-treated with O_2 plasma. The scanning electron microscopy (SEM) images in Figure 1 present the surface and cross-sectional images of the pristine Ti- Fe_2O_3 and oxygen-plasma-treated Ti- Fe_2O_3 (OPT-Ti- Fe_2O_3) photoanodes. Figure 1a,d indicate that the diameter of the Fe_2O_3 nanowire was 40–50 nm while the pristine Ti- Fe_2O_3 film was about 490 nm thick. After treatment at the power of 100 W for 150 s and 200 W for 70 s, the surface morphology of OPT-100W-150s and OPT-200W-70s had no noticeable change in Figure 1b,c, and the thickness of OPT-Ti- Fe_2O_3 films was still about 490 nm in Figure 1e,f.

Crystal structure of the photoanodes was characterized by Raman spectroscopy and X-ray diffraction (XRD). The Raman spectra of the photoanodes are depicted in Figure 2a. Four phonon lines at 222, 288, 405, and 604 cm^{-1} appeared in the three spectra of the photoanodes, which corresponded to the $A_{1g}(1)$, $E_g(2)$, $E_g(3)$, and $E_g(4)$ modes of hematite [16]. There were no obvious differences between the photoanodes with or without O_2 plasma treatment. This demonstrated that plasma treatment has little effect on the crystal structure of the films. XRD patterns of the photoanodes are shown in Figure 2b. Five distinct diffraction peaks of hematite could be observed in the spectra, and these peaks corresponded to the (012), (104), (110), (024), and (330) facets of Fe_2O_3 [17]. There were some other diffraction peaks originated from the Sb: SnO_2 substrate, and no peak related to the Ti dopant was observed. The result demonstrated that the diffraction peaks of Ti- Fe_2O_3 photoanodes had no obvious change after plasma treatment.

We also compared the absorption spectra of the Ti- Fe_2O_3 photoanodes with and without O_2 plasma treatment. The absorption spectra (Figure 2c) of the three films were almost the same. The absorption threshold of the films all appeared at around 600 nm, which corresponded to the bandgap of 2.1 eV [18]. This was consistent with the bandgap of hematite. Based on these results, it can be concluded that the morphology, structure, and optical properties of Ti-doped Fe_2O_3 electrodes change negligibly after O_2 plasma treatment.

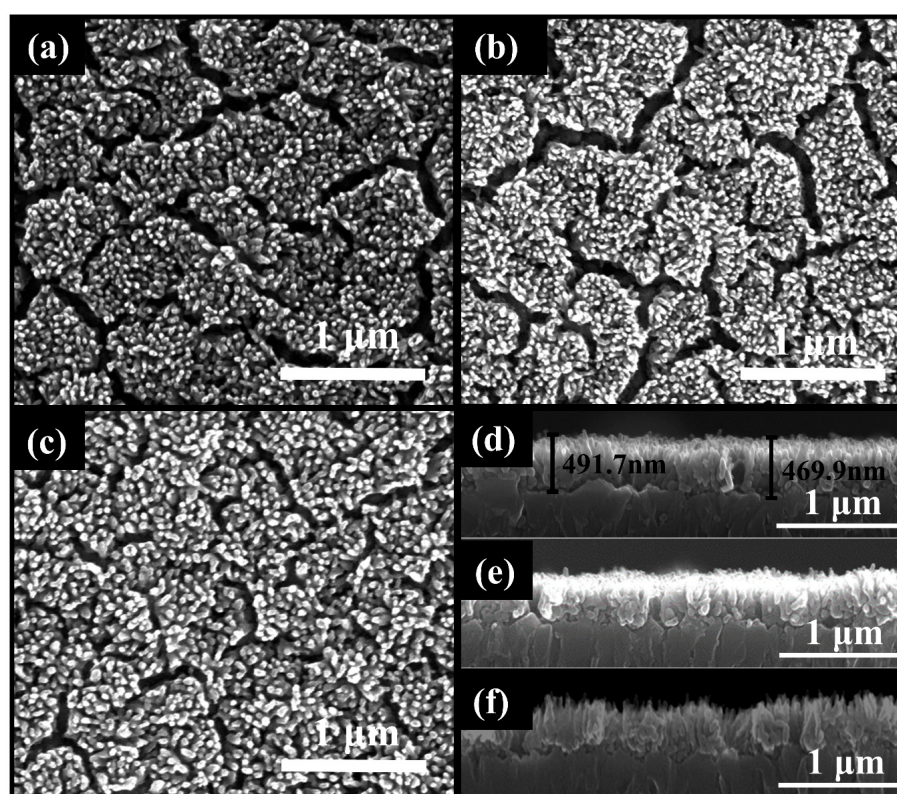


Figure 1. The top-view scanning electron microscopy (SEM) images of (a) pristine $\text{Ti-Fe}_2\text{O}_3$, (b) OPT-100W-150s, and (c) OPT-200W-70s photoanodes; cross-sectional images of (d) pristine $\text{Ti-Fe}_2\text{O}_3$, (e) OPT-100W-150s, and (f) OPT-200W-70s photoanodes.

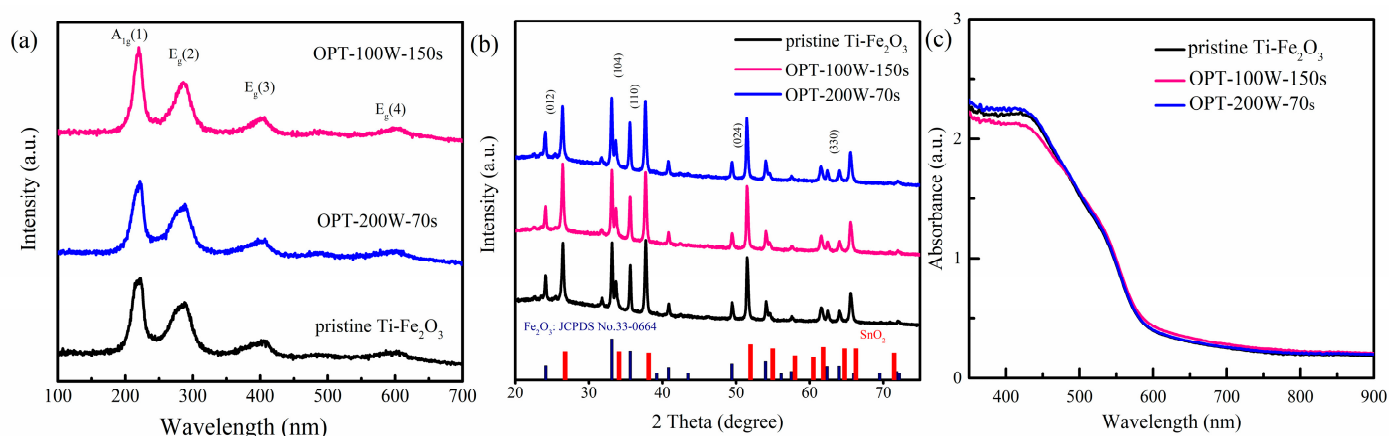


Figure 2. (a) Raman, (b) X-ray diffraction (XRD) patterns, and (c) absorption spectra of pristine $\text{Ti-Fe}_2\text{O}_3$, OPT-100W-150s, and OPT-200W-70s photoanodes, respectively.

2.2. Effect of O_2 Plasma on the PEC Performance of $\text{Ti-Fe}_2\text{O}_3$ Photoanodes

The conditions of O_2 plasma treatment were first optimized. The linear scan voltammetry (LSV) curves of pristine $\text{Ti-Fe}_2\text{O}_3$ and OPT- $\text{Ti-Fe}_2\text{O}_3$ photoanodes were performed in 1 M NaOH ($\text{pH} = 13.6$) aqueous solution at a scan rate of 10 mVs^{-1} , and the results are presented in Figure S1. The optimal films of OPT-100W-150s and OPT-200W-70s treated under different power of O_2 plasma were both selected to investigate the power effect of O_2 plasma treatment on the PEC performance of $\text{Ti-Fe}_2\text{O}_3$ photoanode. The J.-V. curves of pristine $\text{Ti-Fe}_2\text{O}_3$, OPT-200W-70s, and OPT-100W-150s are measured in the electrolyte of 1 M NaOH aqueous solution as shown in Figure 3a. It can be seen that the OPT-200W-

70s photoanode showed the highest photocurrent density of $2.14 \text{ mA} \cdot \text{cm}^{-2}$ at 1.23 V vs. RHE, which was 1.95 times higher than $1.10 \text{ mA} \cdot \text{cm}^{-2}$ of the pristine $\text{Ti-Fe}_2\text{O}_3$. The onset potential of the OPT-200W-70s photoanode exhibited an approximate 50 mV cathodic shift compared with pristine $\text{Ti-Fe}_2\text{O}_3$, which lowered the applied potential to drive the PEC water oxidation reaction. It was also found that the photocurrent of OPT-200W-70s here showed greater superiority for water oxidation than many reported $\text{Ti-Fe}_2\text{O}_3$ nanowires as depicted in Table S1 [5,19–21]. This all suggests that O_2 plasma treatment is an effective method for promoting the PEC water oxidation kinetics of $\text{Ti-Fe}_2\text{O}_3$ photoanodes.

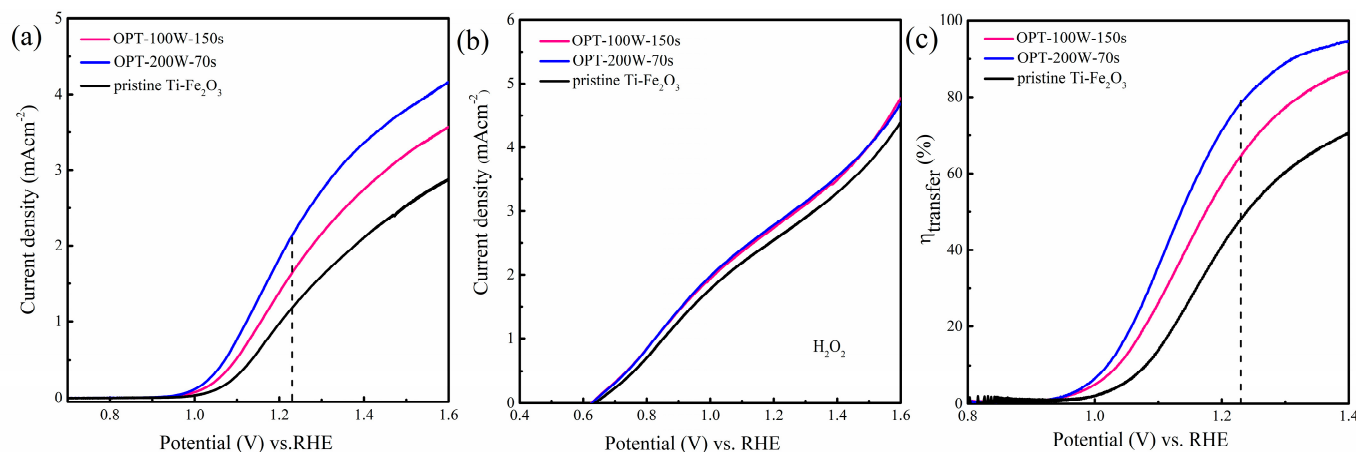


Figure 3. (a) The J-V curves of optimum OPT- $\text{Ti-Fe}_2\text{O}_3$ and pristine $\text{Ti-Fe}_2\text{O}_3$ photoanodes measured in the electrolyte of 1 M NaOH aqueous solution. (b) Linear sweep voltammetry (LSV) scans of OPT-100W-150s, OPT-200W-70s, and pristine $\text{Ti-Fe}_2\text{O}_3$ photoanodes under irradiation in 1 M NaOH aqueous solution with 0.5 M H_2O_2 from 0.4 V to 1.6 V vs. reversible hydrogen electrode (RHE) with a scan rate of 10 mV s^{-1} . (c) Charge transfer efficiency of OPT-100W-150s, OPT-200W-70s, and pristine $\text{Ti-Fe}_2\text{O}_3$.

In addition, the stability of the $\text{Ti-Fe}_2\text{O}_3$ photoanodes was investigated, and the I-t curves of pristine $\text{Ti-Fe}_2\text{O}_3$ and OPT-200W-70s were measured at the constant potential of 1.23 V vs. RHE as depicted in Figure S2. The photocurrent density of the pristine $\text{Ti-Fe}_2\text{O}_3$ photoanode was kept at 1.1 mA cm^{-2} at the duration of 2000 s at 1.23 V vs. RHE. The OPT-200W-70s showed the photocurrent density of 2 mA cm^{-2} at the moment of light on, and then the photocurrent rapidly dropped in the first 500 s. After that, the photocurrent dropped slowly and almost stabilized at 1.72 mA cm^{-2} . Although the photocurrent dropped a little during the measurement process, it was still far higher than the pristine $\text{Ti-Fe}_2\text{O}_3$ photoanode at the same constant potential.

To investigate the effect of O_2 plasma on the surface charge transfer of $\text{Ti-Fe}_2\text{O}_3$ photoanode, we further calculate the hole transfer efficiency from the I-V curves using H_2O_2 as hole scavenger. When adding H_2O_2 in the electrolyte, the photocurrent densities of pristine $\text{Ti-Fe}_2\text{O}_3$, OPT-100W-150s, and OPT-200W-70s tended to be almost the same, as shown in Figure 3b. It can be concluded that the carriers' generation and bulk charge transport in the three electrodes show little difference, because almost 100% of the photo-generated holes are considered to be extracted from the electrodes in the presence of the hole scavenger H_2O_2 in the electrolyte. The practical charge transfer efficiencies (η_{transfer}) of these photoanodes are calculated using the ratio of $J_{\text{H}_2\text{O}}/J_{\text{H}_2\text{O}_2}$, where the $J_{\text{H}_2\text{O}}$ and $J_{\text{H}_2\text{O}_2}$ denote the photocurrent density measured in 1 M NaOH aqueous solution without and with 0.5 M H_2O_2 , respectively. The curves are depicted in Figure 3c [22–24]. It can be seen that OPT-200W-70s and OPT-100W-150s showed higher η_{transfer} of 78% and 64% than the 47% of pristine $\text{Ti-Fe}_2\text{O}_3$ in the measured potential range, which were 1.66 and 1.36 times that of pristine $\text{Ti-Fe}_2\text{O}_3$. These were very close to the 1.95 and 1.5 times enhancements of photocurrents, correspondingly. The result reveals that O_2 plasma treatment significantly increased the surface charge transfer efficiency of the photoanodes.

Electrochemical impedance spectra (EIS) of pristine and OPT-Ti-Fe₂O₃ photoanodes were also measured to further study the charge transport and transfer dynamics at a bias of 1.23 V vs. RHE under illumination conditions. The impedance spectra of the photoanodes are illustrated in Figure 4a, in which the impedance of Ti-Fe₂O₃ treated with plasma is smaller than the pristine one. The impedance of OPT-200W-70s was the smallest. By fitting the EIS data according to the equivalent circuit shown in the inset of Figure 4a, the data of the series resistance (R_s), charge transfer resistance (R_{ct}), the bulk capacitance of hematite (C_{bulk}), and the capacitance of the space charge layer at the interface of Fe₂O₃/electrolyte (C_{sc}) for the electrodes were obtained. The relevant data are listed in Table 1. Compared with the pristine Ti-Fe₂O₃ photoanode, the charge transfer resistance of OPT-200W-70s and OPT-100W-150s photoanodes both decreased, and OPT-200W-70s had the lowest charge transfer resistance. This further indicated that the O₂ plasma treatment improved the surface charge transfer dynamics of the Ti-Fe₂O₃ photoanode. Moreover, the series resistances also decreased a little after O₂ plasma treatment.

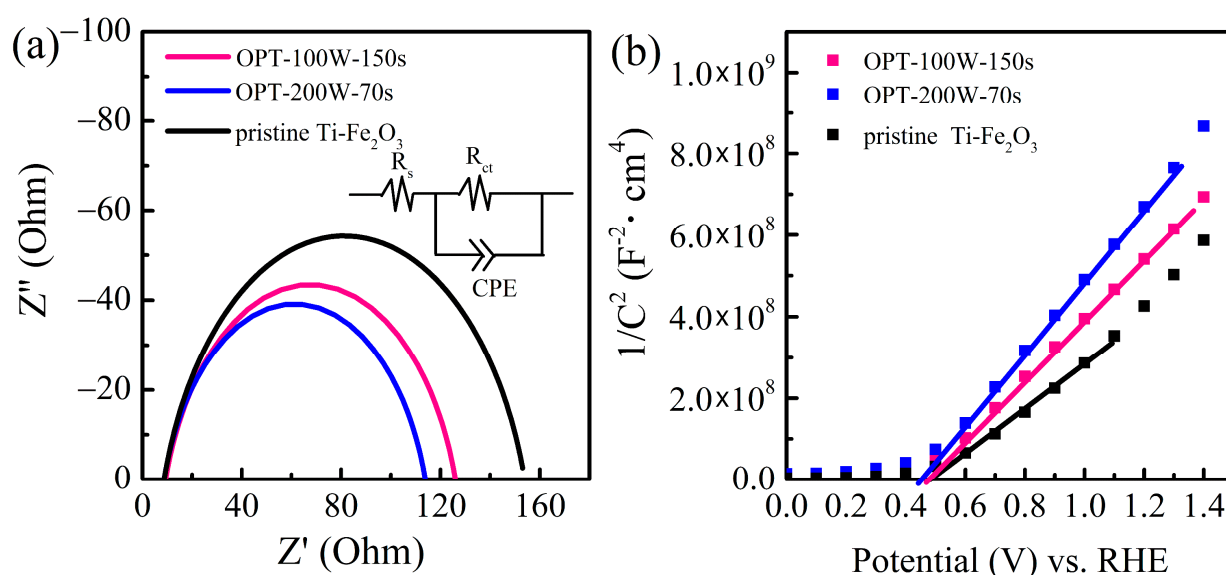


Figure 4. (a) Nyquist plots and (b) Mott-Schottky curves of pristine Ti-Fe₂O₃, OPT-100W-150s, and OPT-200W-70s electrodes. The inset is the equivalent circuit.

Table 1. The fitted equivalent circuit parameters from electrochemical impedance spectra (EIS) data of pristine Ti-Fe₂O₃, OPT-100W-150s, and OPT-200W-70s photoanodes.

Circuit Element	R_s (Ω)	R_{ct} (Ω)	C_{bulk} (F)	C_{sc} (F)
Pristine Ti-Fe ₂ O ₃	9.87	143.49	8.77×10^{-5}	3.98×10^{-4}
OPT-100W-150s	9.66	114.25	9.46×10^{-5}	7.99×10^{-4}
OPT-200W-70s	9.41	103.67	9.48×10^{-5}	7.14×10^{-4}

As the carrier density is an important factor for PEC performance, the Mott-Schottky measurement was taken to understand the effect of O₂ plasma treatment on the carrier densities of Ti-Fe₂O₃ photoanodes. Mott-Schottky curves of the electrodes were all measured at 1 kHz in a dark condition as illustrated in Figure 4b. The effective carrier densities of the electrodes could be calculated according to the equation [25,26]:

$$1/C^2 = \frac{2}{e\epsilon\epsilon_0 N_d} \times (V - V_{FB}) \quad (1)$$

where ϵ , ϵ_0 , e , N_d , V , V_{FB} in the equation represented the permittivity of Fe₂O₃ ($\epsilon = 80$) [27,28], the permittivity of vacuum ($\epsilon_0 = 8.8542 \times 10^{-12}$ F/m), fundamental charge constant

($e = 1.602 \times 10^{-19}$ C), carrier density, applied potential, and flat band potential, respectively [25,29]. The flat band of pristine Ti-Fe₂O₃, OPT-100W-150s, and OPT-200W-70s are approximate 0.49, 0.48, 0.46 V vs. RHE, respectively. The carrier densities of the photoanodes can be calculated by the slopes of the Mott-Schottky curves. For pristine Ti-Fe₂O₃, the carrier density was calculated to be 3.16×10^{19} cm⁻³. The electrodes of OPT-100W-150s and OPT-200W-70s had lower carrier densities of 2.38×10^{19} cm⁻³ and 2.01×10^{19} cm⁻³, respectively. The decreased carrier density may be associated with the decreased donor-type states.

2.3. Mechanism of O₂ Plasma Treatment on Promoting PEC Performance

To explore the impact of plasma on the improved PEC performance, we carried out XPS analysis on the films, because the plasma was a surface treatment strategy that could strongly affect the chemical environment near the surface of the electrode. The Fe 2p spectra of the electrodes are summarized in Figure 5a, in which the peaks appear around 724.78 eV and 711.3 eV, indicating a typical spectrum for Fe 2p_{1/2} and Fe 2p_{3/2} of Ti-doped Fe₂O₃, respectively [30,31]. For Fe 2p_{3/2} peaks, the peak at 711.3 eV and the shoulder at 710.3 eV were attributed to Fe(III)-O and Fe(II)-O, which correspond to Fe³⁺ and Fe²⁺ chemical states, respectively. To further clarify the effect of O₂ plasma treatment, XPS difference spectra were calculated as shown in Figure S3. The negative peaks at about 710 eV in the difference spectra suggest the decreased intensity of Fe(II)-O peak after O₂ plasma treatment. For OPT-200W-70s, the peak of Fe 2p_{1/2} and Fe 2p_{3/2} significantly shifted to the higher binding energy of 725 eV and 711.5 eV, respectively, as listed in Table 2. The Ti 2p XPS spectra of pristine Ti-Fe₂O₃ (Figure 5b) presented the peaks at the binding energy of 458.39 eV and 464.23 eV that were associated with Ti 2p_{3/2} and Ti 2p_{1/2}, respectively [32]. After O₂ plasma treatment, the peaks both gradually shifted to higher binding energy with the increase of the power, and the values are listed in Table 2. OPT-200W-70s exhibited a maximum shift of 0.36 eV for 2p_{3/2} and 0.3 eV for 2p_{1/2}. The result suggests that the O₂ plasma treatment has a great influence on the chemical state of the sample surface.

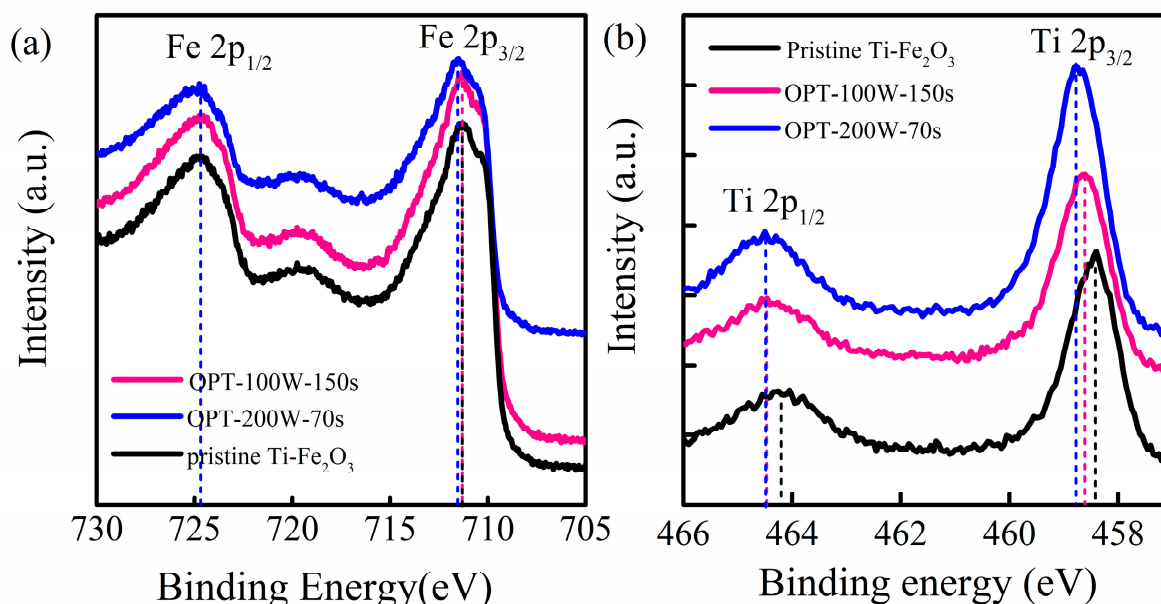


Figure 5. X-ray photoelectron spectroscopy analysis: (a) Fe 2p peaks and (b) Ti 2p peaks of OPT-100W-150s, OPT-200W-70s, and pristine Ti-Fe₂O₃ samples, respectively.

Table 2. The listed binding energy values of Fe, Ti, and O elements in X-ray photoelectron spectroscopy (XPS) spectra for the films of the pristine Ti-Fe₂O₃, OPT-100W-150s, and OPT-200W-70s.

Sample	Binding Energy (eV)				
	Fe 2p _{1/2}	Fe 2p _{3/2}	Ti 2p _{1/2}	Ti 2p _{3/2}	O1s (Main Peak)
Pristine Ti-Fe ₂ O ₃	724.78	711.3	464.23	458.39	530.22
OPT-100W-150s	724.78	711.3	464.53	458.64	530.31
OPT-200W-70s	725	711.5	464.53	458.75	530.45

The deconvoluted peaks for O 1s are depicted in Figure 6. The observed main peak at 530.2 eV and the shoulder peak at approximate 531.8 eV were attributed to the lattice oxygen (denoted as O²⁻) and the defect sites with low oxygen coordination, i.e., oxygen vacancies on sample surface (denoted as O_v) [33–36]. The main peak at 530.2 eV also shifted toward higher binding energy after O₂ plasma treatment, and the maximum shift was about 0.22 eV, as depicted in Table 1. Furthermore, the integrated area of O_v/O²⁻ of the three films was calculated to understand the change in the oxygen-related surface states under different treatment conditions. For pristine Ti-Fe₂O₃, the ratio of O_v/O²⁻ was calculated to be 53.4%. After treatment with O₂ plasma, the ratios of OPT-100W-150s and OPT-200W-70s were decreased to 51.6% and 49.8%, respectively. The values are illustrated in Table 3. The results strongly suggest that O₂ plasma treatment reduced the oxygen vacancies on the surface of Ti-Fe₂O₃ films. Thus, the electron density around Ti and Fe was decreased due to the increase in lattice oxygen, which resulted in the decreased shielding ability and the binding energy moving towards high energy. Combined with the previous discussion, it is believed that the enhanced PEC performance of Ti-Fe₂O₃ was attributed to the reduction of oxygen vacancies at the surface of electrode, rather than the variation in properties such as light absorption, morphology, and crystal structure.

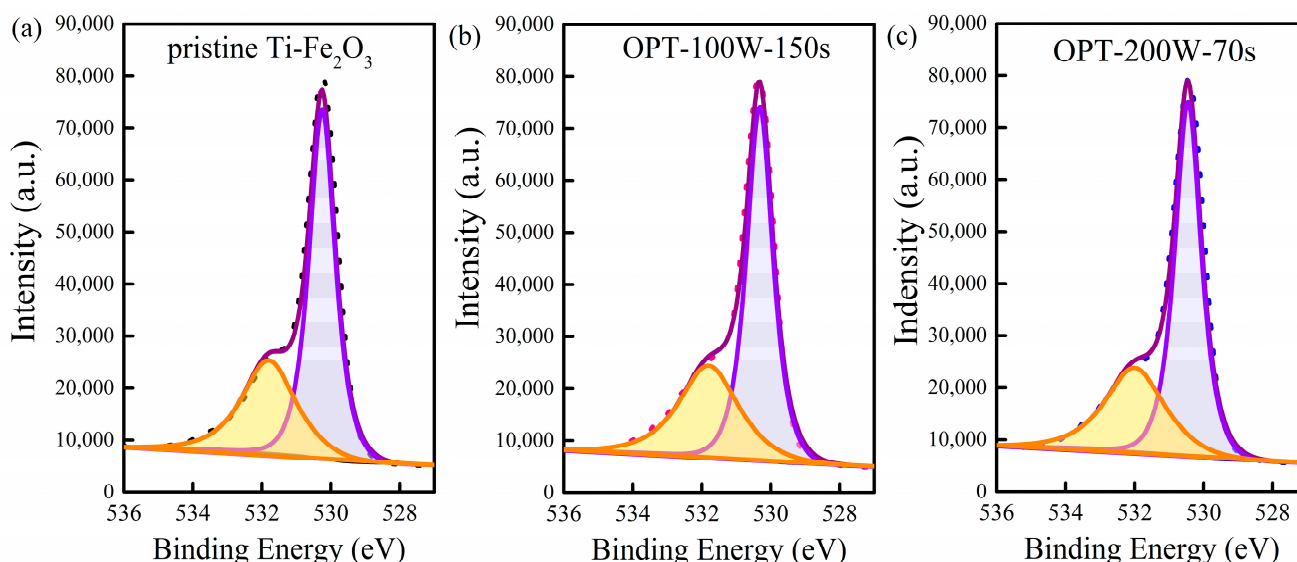
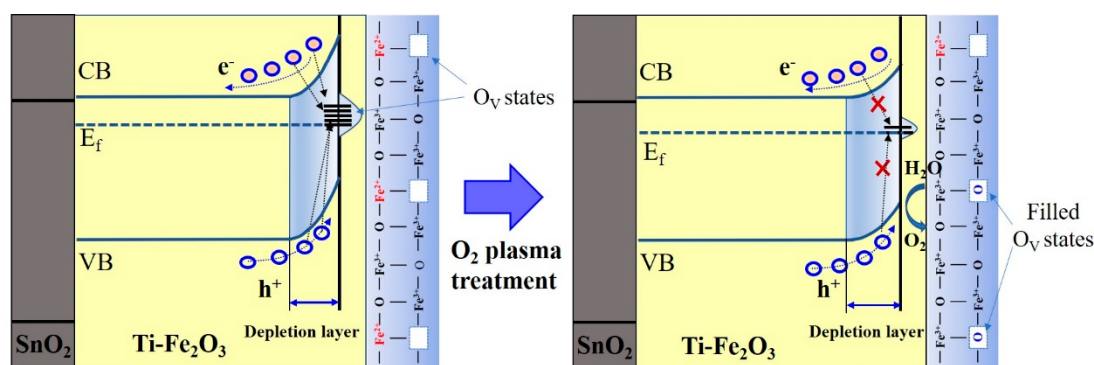
**Figure 6.** X-ray photoelectron spectroscopy of O 1s peaks of (a) pristine Ti-Fe₂O₃, (b) OPT-100W-150s, and (c) OPT-200W-70s samples.

Table 3. The ratio of the integrated area of O_V/O^{2-} in the XPS spectra for the pristine $Ti-Fe_2O_3$, OPT-100W-150s, and OPT-200W-70s samples.

Sample	Ratio of O_V/O^{2-}
Pristine $Ti-Fe_2O_3$	53.4%
OPT-100W-150s	51.6%
OPT-200W-70s	49.8%

Finally, let us discuss the effect of O_2 plasma treatment on the enhanced PEC performance of $Ti-Fe_2O_3$ photoanodes. The Fe_2O_3 nanowire photoanode has a large number of oxygen vacancies on the surface, which will generate extra electrons to reduce Fe^{3+} to Fe^{2+} [37]. When the concentration of oxygen vacancy is too high, Fe^{2+} sites may cause the recombination of photogenerated holes [38], which decreases surface charge transfer properties, and therefore retards the kinetics of hole reaction [15,39]. Furthermore, the oxygen vacancy is difficult to remove as an intrinsic defect. However, O_2 plasma has high reactivity to fill up the oxygen vacancies at the photoanode surface. Thus, the ratio of O_V/O^{2-} is reduced when highly reactive oxygen atoms collide with the photoanodes' surface, which in turn causes the reduction in donor density of the $Ti-Fe_2O_3$ photoanode. The filling of the oxygen vacancy also reduced the amount of Fe^{2+} sites, which was consistent with the decreased intensity of $Fe(II)-O$ peaks in XPS spectra. Therefore, the surface recombination mediated by oxygen vacancies was lowered, and the charge transfer properties were enhanced, leading to a remarkably improved PEC performance, as illustrated in Scheme 1.



Scheme 1. Schematic illustration of the effect of O_2 plasma treatment on the surface oxygen vacancies of Ti -doped Fe_2O_3 . (O_V denotes the surface oxygen vacancies of Ti -doped Fe_2O_3).

Furthermore, the PEC performances had little change under different processing time when the plasma treatment was set as 100 W. This might be because the kinetic energy of oxygen plasma is small, and only a small thickness of the surface layer was affected by the plasma. For the power of 200 W with a greater oxygen plasma kinetic energy, the treatment's depth became deeper. More oxygen vacancies were remedied by extending the treatment time; hence, the PEC performance became better. However, when the time is further increased, the smaller carrier density will result in a smaller surface electric field. This will decrease the charge separation and deteriorate the PEC performance of the photoanodes.

3. Materials and Methods

3.1. Materials

Sodium sulphate ($NaSO_4$, 99%), ferric chloride ($FeCl_3 \cdot 6H_2O$, 99%), and titanium tetrachloride ($TiCl_4$, 99.5%) were purchased from Aladdin Reagent Company (Shanghai, China). Hydrogen peroxide (H_2O_2 , 30%), and sodium hydroxide ($NaOH$, 95%) were obtained from Beijing Chemical Reagent Company (Beijing, China). The fluorine-doped

SnO₂ (SnO₂: F) transparent conducting glass (FTO, resistance: 17 Ω/eq) substrates were from Yingkou OPV Tech New Energy Co. Ltd. (Yingkou, China).

3.2. Preparation of Ti-Doped Fe₂O₃ Photoanodes

3.2.1. Preparation of Ti-Fe₂O₃ Nanowires Array on FTO Substrate

Ti-doped hematite nanowires array films were prepared on FTO conductive glass by the reported hydrothermal method [40]. FTO substrate (1.1 cm × 2.5 cm) was cleaned by the normal method [41]. A 20 mL mixed solution containing 1 M FeCl₃·6H₂O and 1 M Na₂SO₄ was prepared first, and then 0.5 mL TiCl₄ ice water with a concentration of 40 mM was added. Then FTO substrate was put into a Teflon-lined stainless steel autoclave that was filled with 2.5 mL solution. The reaction was performed at a temperature of 120 °C for 4 h, and Ti-doped FeOOH nanowires array with yellow color were obtained. After rinsing with deionized water, the films were annealed by rapid thermal annealing at 800 °C for 30 s, and Ti-FeOOH films were transformed to Ti-Fe₂O₃ nanowires.

3.2.2. O₂ Plasma Treated Ti-Doped Hematite Nanowires

The oxygen gas plasma treatment was performed using a PE-ALD (Jiaxing Kemin electronic equipment Technology Company, KMT-500s, Jiaxing, China) equipped with a radio frequency coil with adjustable power. The O₂ plasma treatment (OPT) was performed with the power of 100 W for different times (90 s, 150 s, and 210 s), and 200 W for 50 s, 70 s, and 90 s at the temperature of 100 °C. O₂ OPT-Ti-Fe₂O₃ film at 150 °C with the power of 150 W for 90 s was also performed for comparative study. The samples were hereafter denoted as pristine Ti-Fe₂O₃, OPT-100W-90s, OPT-100W-150s, OPT-100W-210s, OPT-200W-50s, OPT-200W-70s, OPT-200W-90s, OPT-150 °C-150W-90s. The characterization and the PEC measurement of the samples are presented in the supporting information.

4. Conclusions

The study demonstrated that the PEC performance of Ti-doped Fe₂O₃ nanowire photoanodes was remarkably improved after surface treatment with O₂ plasma. O₂ plasma treatment decreased the oxygen vacancies at the surface of Ti-Fe₂O₃ nanowire films by 6.7% (from 53.4% to 49.8%). The charge transfer of Ti-Fe₂O₃ nanowire photoanodes was improved by 1.66 times via reducing the losses caused by the oxygen vacancies' related recombination. At 1.23 V vs. RHE, the photocurrent density of O₂ OPT-Ti-Fe₂O₃ at the power of 200 W for 70 s reached 2.14 mAcm^{−2}, which was 1.95 times that of the pristine Ti-Fe₂O₃. O₂ plasma treatment is demonstrated to be an effective strategy to improve the charge transfer ability at the surface of Ti-doped Fe₂O₃ photoanode. We believe that further optimizations of the O₂ plasma conditions should lead to even more efficient electrodes, and it can also be applied to tune the surface states and promote the PEC performance of other semiconductor photoelectrodes.

Supplementary Materials: The following are available online at <https://www.mdpi.com/2073-4344/11/1/82/s1>, Figure S1: Current-potential (J-V) curves of (a) pristine Ti-Fe₂O₃, OPT-100W-90s, OPT-100W-150s, and OPT-100W-210s photoanodes. (b) Current-potential (J-V) curves of pristine Ti-Fe₂O₃, OPT-200W-50s, OPT-200W-70s, and OPT-200W-90s photoanodes. The I-V curves are measured with the scan rate of 10 mVs^{−1} from 0.7 V to 1.6 V vs. RHE under irradiation; Figure S2: I-t curves of pristine Ti-Fe₂O₃ and OPT-200W-70s photoanodes; Table S1: The structure, fabrication method, and photocurrent density of some reported works on Ti-doped α-Fe₂O₃ nanowires photoanodes.

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