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3**Plasma-implanted Ti-doped hematite photoanodes with enhanced photoelectrochemical water oxidation performance**

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article info Article history: Received 4 December 2020 Received in revised form 6 February 2021 Accepted 1 March 2021 Available online 6 March 2021 Keywords: Hematite Photoelectrochemistry Surface engineering Plasma ion implantation abstract Hematite (α-Fe_2O_3) is recognized as a promising photoelectrode material for photoelectrochemical (PEC) water splitting, as a result of its abundance, non-toxicity, suitable bandgap, and photochemical stability. Nevertheless, the undesirable physical and photophysical behaviors, such as poor conductivity, short dif- fusion length, and rapid charge-carrier recombination, seriously restrict PEC water splitting efficiency of hematite semiconductors. Herein, we fabricate nanoporous titanium (Ti)-doped α-Fe_2O_3 thin films by a facile hydrothermal reaction, subsequently utilizing energetic plasma ion implantation with a post-an- nealing process to significantly enhance the photoelectrochemical water oxidation performance of hema- tite. On the basis of materials characterization and electrochemical analysis, the optimized Ti-doped Fe_2O_3, i.e., Ti-4-Fe_2O_3, exhibits improved photocurrents of 0.55 and 1.07 mA cm^{-2} at 1.23 and 1.5 V versus RHE respectively under illumination of 100 mW/cm^2 with AM 1.5 G spectrum, showing approximately 1.6-fold increases compared to pristine Fe_2O_3. We attribute this increase to improved charge carrier transport in- duced by Ti doping that reduces the recombination of light-driven charge carriers. The work utilizing plasma-assisted doping technique provides new insights into the surface engineering of photo-responsive semiconductors for the development of emerging hydrogen technologies. 1. Introduction Solar energy has been recognized as one of the most promising and cost-competitive renewable energy alternatives for the re- placement of conventional fossil fuels. Photoelectrochemical (PEC) water splitting is an attractive approach to convert renewable light energy into chemical energy for practical applications, owing to the facile storage and transportation of hydrogen. In the field of solar water splitting, we still face the challenge related to the cost- ⁎

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. effective fabrication of robust photo-responsive materials with high performance in an economic way. Among the most favorable semi- conductors, e.g. $BiVO_4$, WO_3 and Fe_2O_3 for PEC water oxidation, there is no doubt that

22**hematite (α-Fe_2O_3) is a promising** photoanode **candidate** as a result **of its**

chemical stability, environmental friendliness, earth abundance as well as a suitable bandgap (~

11**2.1 eV**) that achieves **a theoretical solar-to-hydrogen efficiency of** ~16% [**1**

].

10**Despite these advantages, hematite suffers from**

ultrafast

35**electron- hole** recombination (**~10 ps), short hole diffusion length (2–4 nm**) and slow **oxygen evolution reaction (OER**

) activity [2]. Various strategies have been developed to overcome these obstacles. Elemental doping is a highly practical approach

15**to improve the PEC performance**. Among various elements, **e.g**. Ti [3], **Sn**

[4], and P [5], titanium doping of hematite photoanodes is a potential strategy. For instance, Franking et al. demonstrated that the addition of Ti precursor solutions on hematite films followed by annealing in atmosphere could promote Ti diffusion into hematite, resulting in the enhancement of its PEC response [6]. Ion

implantation is an efficient technique for surface modification of conventional materials, such as alloys and polymers, to improve their mechanical properties (e.g. anti-corrosion, anti-wear and strength) and chemical properties (e.g. destruction and formation of chemical bonds) [7]. In recent years, the ion implantation technique has been introduced to modify and develop photoelectrodes. For example, Shen's group has reported that V [8], Cu [9] and W [10] ions could be implanted into ZnO lat- tices. The

9**enhanced PEC performance of the** ion implanted **ZnO**

could

21**be attributed to** both **improved visible light absorption and increased charge carrier density**

. Controllable amounts of elemental doping and modification of surface morphology can both be realized by ion implantation. Herein, we fabricate efficient photoresponsive materials by utilizing this technique

15**for improving the performance of PEC water splitting**

for hematite. After different doses of titanium implantation and subsequent post-annealing treatments, pristine and titanium plasma implantation treated hematite, i.e., Fe2O3, Ti-1-Fe2O3, Ti-2-Fe2O3, Ti- 4-Fe2O3 and Ti-8-Fe2O3, were synthesized. The surface morphology of titanium plasma implantation treated hematite is moderately changed to the nanoporous structure. We observe well-distributed Ti doping on the surface, resulting in lower photoluminescence (PL) intensity as a result of reduced charge carrier recombination. The optimized Ti-implanted hematite, Ti-4-Fe2O3, exhibits the lowest charge transfer resistance and highest charge carrier density, re- sulting in a highest photocurrent density with a better stability compared to pristine hematite. To the best of our knowledge, this is the first report of hematite treated by using Ti plasma implantation for the enhancement of PEC water oxidation. 2. Experimental 2.1. Reagents and materials Anhydrous FeCl3 (99%, Alfa Aesar) and NaNO3 (99.9%, DUKSAN) were used as received without further purification. Fluorine-doped tin oxide (FTO) coated glass (6–9 Ω/sq) was sliced to 1.5 × 3.0 cm pieces which were subsequently sonicated in

12**deionized water, acetone and ethanol** each **for 20 min and then dried with**

com- pressed air before use. Ti rods (99.9999%, Shenzhen Morgan Sputtering Targets & Technology Co., China) were used as an ion beam source for implantation. All solutions were prepared using ultrapure water generated by Milli-Q water purification system. 2.2. Preparation of pristine α-Fe2O3 and titanium ion implanted α-Fe2O3 Hematite

11**films were fabricated on fluorine-doped tin oxide (FTO) coated glass according to previous**

studies [11]. Typically, 2.433 g of FeCl3 (0.15 M) and 8.50 g of NaNO3 (1 M) were dissolved in ultrapure water and the volume was adjusted to 100 mL using a 100-mL vo- lumetric flask. The pH of the solution was about 1.5 without the adjustment. After that, 20 mL of the precursor solution was added into each 30 mL Teflon liner containing a piece of FTO glass with FTO side facing down. The hydrothermal reactors were

19**heated at 95 °C for 4 h in an oven**. Consequently, akaganeite (β-**FeOOH**) coated **on FTO**

glass could be obtained and was rinsed with ultrapure water several times. Next, the

12**β-FeOOH was** calcined **at 550 °C for 2 h**

(ramp rate 2.5 °C min−1) and then at 800 °

30**C for 10 min (ramp rate** 5 °**C min−1**) under air atmosphere **to**

obtain α-Fe2O3 in a tube furnace. For titanium ion implantation treatment, the obtained β-FeOOH films were firstly treated with titanium ion beam generated from a metal vapor vacuum arc source by a broad-beam

1**high energy ion implanter** (Model **HEMII-80, Plasma Technology Ltd**

.). Titanium ions were implanted with doses of 0 (a control sample), 1 × 1016, 2 × 1016, 4 × 1016 and 8 × 1016 atoms per centimeter square of the film at a voltage of 35 kV. The obtained materials were named as FeOOH, Ti- 1-FeOOH, Ti-2-FeOOH, Ti-4-FeOOH and Ti-8-FeOOH, respectively. Afterwards, the titanium ion implanted β-FeOOH films were an- nealed under the same condition (

12**550 °C for 2 h and** then 800 °**C for 10 min) to**

get titanium ion implanted α-Fe2O3. The as-prepared films were labeled as Fe2O3, Ti-1-Fe2O3, Ti-2-Fe2O3, Ti-4-Fe2O3 and Ti-8- Fe2O3, respectively. 2.3. Film characterization The surface morphology of titanium ion implanted β-FeOOH and α-Fe2O3 were imaged by a ZEISS EVO MA10 SEM at a voltage of 15 kV.

21**XRD patterns were** collected using **a PANalytical X**′Pert3 **X-ray**

dif- fractometer between 10 and 70 degree with a tension of 40 kV and a current of 40 mA under Cu-Kα radiation (1.54 Å).

24**Raman spectra were** taken **using a** HORIBA HR800 **Raman microscope with a** 514-**nm laser**

. XPS analysis was carried out using a Thermo Fisher ESCALAB 250Xi X-ray photoelectron spectrometer, and the binding energy was calibrated by the C 1s peak at 284.6 eV.

7**Transmission electron microscope (TEM; JEOL** JEM-2100 F) **equipped with energy- dispersive** spectrometer (**EDS**

) was used to explore the elemental distributions and morphological changes. UV–visible absorption spectra were measured using a Shimadzu UV-3600 spectro- photometer equipped with an integrating sphere in the range from 800 to 300 nm. Photoluminescence (PL) spectra were collected with a 500-nm long-pass filter under an excitation wavelength of 450 nm by a Shimadzu RF-5301 PC spectrometer. 2.4. Electrochemical measurements All the electrochemical tests were carried out with a electro- chemical workstation (CHI 760E, Shanghai Chenhua Instruments Co., China) using a three-electrode system in which pristine or titanium ion implanted Fe2O3 film were

18**used as** a **working electrode, Pt wire as counter electrode, and Ag/AgCl** (in 3 M **KCl**

) connected to elec- trolyte (1 M NaOH, pH 13.6) by a salt bridge (3 M KCl) as reference electrode. The electrolyte was purged with nitrogen for 10 min be- fore all the following tests to prevent oxygen reduction reaction at the counter electrode. A working area of 0.283 cm2 of the photo- anodes was irradiated under 1-sun (100 mW/cm2, AM 1.5 G) illu- mination, which used

7**a 300-W xenon lamp with** an **AM 1.5 filter as light source**

for linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), Mott-Schottky (MS) and ampero- metric i-t (I-t) measurements. LSV measurements were conducted to evaluate the PEC water oxidation performance of the as-prepared titanium implanted α- Fe2O3. The

9**potential was** scanned **from −0**.6 **to 0**.6 **V versus Ag/AgCl at a** scan **rate of 10 mV s−1. The**

potential versus Ag/AgCl was con- verted to the potential versus

17**reversible hydrogen electrode (RHE) according to the** following equation: **ERHE = EAg/AgCl + EAg/AgCl 0**.059 pH + × **where ERHE** is **the** converted **potential versus RHE**, E⊖Ag/**AgCl is the** standard electrode **potential** of Ag/**AgCl**

electrode against standard hydrogen electrode and equal to 0.210

8**V at 25 °C, and EAg/AgCl is the experimentally measured potential** versus **Ag/AgCl electrode. For**

EIS tests, an initial potential was set at 0.22

26**V versus Ag/AgCl** (equal **to 1**.23 **V versus RHE**

) with the frequencies ranging

18**from 105 to 0**.5 **Hz** and an **amplitude** voltage **of 10 mV** under illumination. **The**

collected EIS data were fitted using ZView software (Scribner and Associates Inc., USA). MS plots were collected at a frequency of 1 kHz

9**from −0**.6 **to 0**.4 **V versus Ag/AgCl at** an amplitude **of** 5 **mV** under dark Scheme **1**. Fabrication process **of**

titanium ion implanted α-Fe2O3. condition. Charge carrier densities can be estimated according to the following equation: d (c12) 1 Nd = oA2e 2 × dV where Nd is donor density (in m−3), ε is relative permittivity (ε = 80 for hematite [12]), εo is vacuum permittivity (εo = 8.

11**85 × 10−12 F m−1), A is** the surface **area**

(A = 2.83 × 10−5 m2 in this study),

34**e is** electronic **charge (e = 1.602 × 10−19 C**), c **is**

interfacial capacitance (in F), and V is the applied voltage (in V). Amperometric i-t measurements were used to assess the stability of titanium ion implanted α-Fe2O3. During the I-t tests, the bias potential was set at 0.22

26**V versus Ag/ AgCl** (equal **to 1**.23 **V versus RHE**

) and the measurements lasted for 5 h under illumination. A steady nitrogen flow was supplied into the cell to prevent oxygen from entering the electrolyte.

19**3. Results and discussion The fabrication process of**

titanium plasma implanted hematite photoanodes is depicted in Scheme 1. For the preparation of titanium implanted α-Fe2O3, β-FeOOH films were first grown on FTO glass by using a conventional hydrothermal reaction. Afterwards, the β-FeOOH films were treated with different doses of titanium ions, subsequently converting to α-Fe2O3 by a post-annealing process under atmospheric conditions. Pristine hematite as a controlled photoanode was also synthesized in the absence of ion implantation treatments. As shown in the photographs of Supplementary Fig. S1, the color of β-FeOOH films changed from yellow to dark brown in a dose- dependent manner after titanium ion implantation treatment. The uniform color also implies well-distributed Ti ions in the β-FeOOH film. All the treated β-FeOOH films turned to red after the post-annealing process

2**at 550 °C for 2 h and** subsequently **at** 800 °**C for** 10 **min in** order to recover **the** damage of lattice structure caused by ion implantation. As depicted in Fig. S2a–e, we observed that ion beam treatment could cause dose-dependent agglomeration of β- FeOOH nanorods and the formation of porous structures in the process. After calcination (Fig. 1a–e), the SEM images of titanium ion implanted α-Fe2O3 reveal that the aggregation of nanostructures give rise to large porous structure. The lateral feature size of nano- porous structures increases from 130 ± 20 nm in untreated Fe2O3 to 170 ± 20 nm in Ti-8-Fe2O3, depending on the amounts of implanted ions. Notably, the featured sizes have a significant influence on the functional properties of nanomaterials. With the report of Brillet et al. [13], hematite nanorods have been regulated to obtain a de- sired featured size of approximately 30–40 nm using a solution- based encapsulation strategy. They also indicated that smaller nanostructures are beneficial to electron-hole transfer at semi- conductor/liquid interfaces under a high bias potential, in spite of the fact that small nanostructures have negative impacts on the onset potential. Because morphological change of titanium ion im- planted α-Fe2O3 is not evident, we expect the PEC performance of hematite through morphology engineering would be modestly af- fected by ion implantation process. The XRD patterns of the materials, shown in Fig. 2a, indicate the presence of β-FeOOH before the post-annealing process. Two peaks at 11.8 and 35.2 degree are attributed to the diffraction of (110) and (211) facets of akaganeite (JCPDS No. 34–1266), respectively. High intensity of the diffraction peak at 35.2 degree implies that the growth of these nanorods is along the [211] direction [11]. After ti- tanium ion implantation, all diffraction peaks of β-FeOOH sharply decreased (Magnified in Fig. S3a–b), suggesting

3**that Ti atoms have** been implanted **into the lattice** structure **of**

β-FeOOH, which causes disorder in the crystal structure. After calcination at high tempera- ture, the XRD patterns of as-prepared materials (Fig. 2b) reveal the generation of α-Fe2O3 (JCPDS No. 33-0664). The peaks at 35.6 degree are ascribed to the diffraction of (211) facet [11]. Remarkably, al- though these peaks appeared in titanium ion implanted α-Fe2O3 after post-annealing, their intensities decreased compared to that of pristine α-Fe2O3 (Fig. 2c). Additionally, the XRD results do not exhibit the existence of TiO2 or ilmenite in both β-FeOOH and α-Fe2O3. Raman spectra of titanium ion implanted α-Fe2O3 (Fig. 3) have been characterized to further explore the change in crystal structure of titanium ion implanted α-Fe2O3. The intrinsic Raman peaks at 224 (A1g(1)), 243 (Eg(1)), 292 (Eg(1)), 298 (Eg(1)), 410 (Eg(1)), 497 (A1g(2)) and 610 (Eg(1)) cm−1 can be clearly detected from both pristine α-Fe2O3 and titanium ion implanted α-Fe2O3 [14]. Furthermore, the increased intensity of the peak at 660 cm−1 is attributed to the dis- order-sensitive mode (Eu) of α-Fe2O3. This mode is theoretically not Raman-active in the Raman responses of hematite, while it is Fig.

7**1. SEM images of** titanium ion implanted **α-Fe2O3**

at different doses: (a)

7**Fe2O3, (b) Ti**-1-**Fe2O3, (c) Ti**-2-**Fe2O3, (d**

) Ti-4-Fe2O3 and (e) Ti-8-Fe2O3. recognized as a Eu(LO) mode in the infrared measurements [14]. Despite that, imperfect surface symmetry and stress-induced defects (e.g., impure atoms in lattices) can activate strong responses at 660 cm−1. Our Raman results are similar to that of Si-doped hema- tite, implying

22**the incorporation of Ti atoms into the lattice of α-Fe2O3**

[15]. In addition, we further observed a maximum intensity

8**ratio of** the **peak at** 660 **cm−1 to the peak at** 610 **cm−1**

in Ti-4-Fe2O3 (Table S1), which suggests a high degree of asymmetry in the bulk structure as well as considerable amounts of Ti doping in α-Fe2O3. The full survey and high-resolution XPS spectra including O 1s, Fe 2p and Ti 2p of the Ti-4-Fe2O3 specimen were characterized (Fig. 4). In the survey spectrum (Fig. 4a), in addition to Fe and O, the ele- ments including Ti, Sn, and C can also be detected. The detectable amount of Sn is possibly attributed to the diffusion of Sn from the FTO glass at high temperature [16]. The existing Ti atoms are arising from the dopants generated by titanium plasma implantation. The C 1s signal as a binding energy reference can be detected due to ad- ventitious carbon contamination during air exposure. The Fe 2p high-resolution spectrum (Fig. 4b) shows two split spin-orbit com- ponents, Fe 2p1/2 and Fe 2p3/2, located at 724.3 and 710.7 eV, re- spectively, which are quite consistent with their reported binding energies in α-Fe2O3 [17]. Besides,

29**the binding energy difference between** the **two components is** 13.5 **eV**

, clearly verifying the for- mation of Fe2O3 [18]. Additionally, surface

16**peaks for Fe 2p1/2 and Fe 2p3/2** with high **binding** energies **of** 728.1 **and** 714.5 **eV**

have been fitted. These surface peaks could be induced by disordered atomic arrangement at the surface of materials, which probably gives rise to low electron density surrounding the Fe(III) atoms, thus requiring high energy to eventually produce photoelectrons [19]. The oxida- tion state (i.e., Fe3+) of the Fe has been confirmed by the satellite peaks of Fe 2p1/2 and Fe 2p3/2 at 732.7 and 718.2 eV, respectively [20]. The O 1s spectral region in Fig. 4c can be fitted with

32**two peaks located at 530.0 and 531**.4 **eV**, which can **be** assigned **to** lattice oxygen (Fe–**O) and** surface **hydroxyl (O**–H), **respectively**

[21]. Im- portantly, the Ti 2p high-resolution spectrum (Fig. 4d) displays two components, Ti 2p1/2 and Ti 2p3/2, with binding energies of 464.0 and 458.3 eV, respectively, indicating Ti(IV) atoms surrounded by oxygen atoms [22]. The difference of binding energies between

29**two split spin-orbit components is 5**.7 **eV**

, re-confirming the oxidation state (i.e., Ti4+) of the implanted titanium atoms [23]. The two shake-up peaks at 465.0 and 459.4 eV presumably result from reduced kinetic energy of photoelectrons [24]. XPS depth profiling was also per- formed to analyze elemental distribution in the implantation di- rection. The profile of Ti-4-FeOOH reveals that titanium atoms can Fig. 3. Raman spectra of titanium ion implanted α-Fe2O3 at different doses. Fig. 2. XRD patterns of titanium ion implanted materials at different doses. (a) ion implanted β-FeOOH, (b) ion implanted α-Fe2O3 after post-annealing, and (c) magni- fied view of (211) peaks for ion implanted α-Fe2O3. be implanted into β-FeOOH film at a depth of at least 180 nm (Fig S4). After the post-annealing process under atmospheric con- ditions for the formation of Ti-4-Fe2O3, more oxygen atoms were introduced into the film which can be observed by the increased oxygen percentage (Fig. 4e). The Ti/Fe atomic ratio of ~ 0.15 is also indicates a well-distributed Ti doping in the depth direction (Fig. 4f). The atomic percentage of iron at the surface is low probably because of carbon contamination. The incorporation of Ti atoms into plasma ion implanted β- FeOOH and α-Fe2O3 was further investigated by TEM and corresponding mapping techniques. As shown in Fig. 5a, the TEM results indicate that Ti-4-FeOOH has a nanorod structure with a diameter of around 80 nm (solid blue line). Additionally, EDS mapping was used

33**to evaluate the influence of** direct **Ti** bombarding on **the**

spatial distribution of Fe, O and Ti elements. The signal of element Ti has been observed in an extended area of Ti-4-FeOOH, indicating that the energetic ion implantation technique enables the penetration of Ti atoms into the deep area of the material, which is consistent with the results of XPS depth profile. Besides, the mapping images also present evenly distributed Fe and O atoms in the nanostructured Ti- 4-FeOOH. After annealing the material in synthetic air, the obtained Ti-4-Fe2O3 displays an aggregated bulk-like nanostructure (Fig. 5b). The elemental mapping of Ti-4-Fe2O3 clearly reveals the presence of Ti with Fe and O, where a well-distributed Ti element has been observed in a width of ca. 400 nm. The optical absorption properties of pristine and titanium ion implanted Fe2O3 films were evaluated by UV–visible absorption spectroscopy (Fig. 6a). The spectra with an absorption onset at 600 nm exhibit a typical characteristic of hematite films. The Tauc plot (αhv)1/r ~ hv, where α represents

8**absorption coefficient of the** material; **h is Planck constant; v is frequency of** photon; **and** r **is**

the nature of the transition and equal to 2 for indirect allowed transi- tions, can be used to estimate the bandgap of semiconductors [1]. As shown in the inset table of Fig. 6b, Tauc plots derived from the absorption spectra of as-prepared α-Fe2O3 (Fig. 6b) yield bandgaps that are largely independent of titanium ion implantation treatment, revealing an indirect bandgap of 2.05–2.06 eV for all the α-Fe2O3, which is in accordance with previous literature [3]. The Ti-dopped semiconductor

1**still retained more than 95% of the initial absorption after** 35 **days of exposure**

. Photoluminescence (PL) spectra of as- prepared pristine and titanium ion implanted α-Fe2O3 films were carried out under an excitation wavelength of 450 nm to monitor the recombination of charge carriers in the bulk and at the surface (Fig. S5). The PL emission recorded from 520 to 750 nm exhibits a broad emission peak at around 620 nm for both pristine α-Fe2O3 and titanium ion implanted α-Fe2O3, which is in line with previous re- port [25]. The PL emission, which is mainly attributed to the re- combination of photogenerated electrons and holes, could serve as an indicator to indirectly evaluate the efficiency of charge carrier transport [26]. As shown in Fig. S5, Ti-4-Fe2O3 shows the lowest PL intensity, suggesting suppressed recombination of photogenerated charge carriers due to improved diffusion rate [27], potentially leading to the enhancement of photoactivity. Further investigation on the reduced charge recombination centers in Ti-incorporated Fig. 4. XPS spectra collected from Ti-4-Fe2O3: (a) full survey, (

16**b) Fe 2p, (c) O** 1 s, (**d) Ti 2p, (e**) depth profile **and (f**

) Ti/Fe atomic ratio. hematite is of importance to understand the roles of doping in photoelectrodes. The charge transfer characteristic of these titanium ion im- planted α-Fe2O3 photoanodes was explored by electrochemical im- pedance spectroscopy (EIS). As shown in the Nyquist diagram (Fig. 7a), the EIS spectra were fitted based on the equivalent circuit in the inset of Fig. 7a using Zview software [28]. The 1-RC equivalent circuit model contains a RC circuit, including a charge transfer re- sistance at electrode||electrolyte interface (Rct), a parallel double- layer capacitance (CPE), as well as a series resistance (Rs). As listed in fitting results of Table S2, hematite implanted with different doses of titanium show lower charge transfer resistance compared to that of Fig. 5. TEM and corresponding TEM-mapping images of (a) Ti-4-FeOOH and (b) Ti-4-Fe2O3. pristine α-Fe2O3, indicating that implantation-induced Ti-doping could facilitate the injection of charge carriers into electrolyte and hence enhance the performance of PEC water oxidation [29]. Among them, the optimized Ti-implanted hematite, Ti-4-Fe2O3, exhibits the smallest arc radius, illustrating lowest charge transfer resistance in the system. Moreover, the charge carrier densities of titanium ion implanted α-Fe2O3 were analyzed by Mott-Schottky (MS) measure- ments (Fig. 7b). The positive slopes in the MS plots

28**reveal the n-type** behavior **of these photoelectrodes. The**

donor densities of these semiconductors have been estimated by the slopes of the MS plots (Table S3). Among all the photoanodes, Ti-4-Fe2O3 presents the highest charge carrier density of 7.1 × 1026 m−3, which shows a 7.4- time increase in comparison to the pristine α-Fe2O3. The increased donor density is beneficial to the conductivity of hematite, thereby improving the collection efficiency of light-driven charge car- riers [16,30].

28**To evaluate the effectiveness of** titanium ion implantation, **the photocurrent density-potential**

curves (i.e., LSV curves) of untreated and ion implanted α-Fe2O3

7**were conducted** using **a three-electrode configuration**

in a self-designed electrochemical system (Fig. S6). While the pristine α-Fe2O3

36**exhibits a low photocurrent density of 0**.34 **mA cm−2 at 1.23 V** versus **RHE**

under irradiation, Ti-implanted α- Fe2O3 with a dose of 4 × 1016 atoms cm−2 treatment (i.e., Ti-4-Fe2O3) reaches a maximum photocurrent density of 0.55 mA cm−2, a ~1.6 times increase compared to pure hematite (Fig. 7c), which is consistent with the result of EIS and MS measurements. The pho- tocurrent densities of untreated and Ti-implanted α-Fe2O3 with different ion doses at

15**1.23 V and 1.5 V** versus **RHE** are summarized **in** Table S4. **The**

dark current of Ti-dopped semiconductor

1**was almost no change after 10 days. The degradation of PEC performance for**

Ti-dopped semiconductor

1**was much slower (<5%) for the films stored under 0% RH and 50% RH after 30 days of exposure**

. The Fig. 6. (a) UV–visible absorption spectra of titanium ion implanted α-Fe2O3, and (b) Tauc plots of titanium ion implanted α-Fe2O3 for the determination of the bandgaps. Fig. 7. Electrochemical measurements of pristine and Ti-implanted α-Fe2O3 at different doses: (a) electrochemical impedance spectroscopy (EIS) spectra, (b) Mott-Schottky (MS) plots, (c) linear sweep voltammetry (LSV) curves, and (d) amperometric (I-t) tests. amperometric (I-t) measurements were performed

3**at a bias** poten- tial **of 0**.22 **V versus Ag/AgCl**

(equal to 1.23 V versus RHE) to in- vestigate the stability of pure and Ti- implanted α-Fe2O3. As shown in Fig. 7d, the photocurrent of untreated α-Fe2O3 and as-prepared Ti plasma treated α-Fe2O3 gradually decreased in the 5-h measure- ment. Among ion implanted hematite, Ti-4-Fe2O3 preserves 65% of the initial photocurrent with the best

24**current density of ~0.4 mA cm−2**

after 5-h illumination, which is approximately twice as high as that of untreated α-Fe2O3. Titanium incorporation is known

3**to improve the PEC water** oxi- dation **performance of hematite**

nanostructures. Previous efforts on Ti doping strategies include hydrothermal reaction [31], solution- based deposition-annealing process [11],

3**atomic layer deposition assisted solid-state diffusion**

[32], and molecular beam epitaxy growth [33]. Compared with these methods, our plasma ion im- plantation strategy provides the opportunity to control the amount of Ti doping in the photo-responsive materials. The PEC performance of hematite is overall determined by three processes: photon ab- sorption, charge carrier separation and surface charge transfer. Our UV–visible absorption results together with previous works reveal

3**that Ti doping has little influence on the** bandgap **of hematite**

[31a,34]. In addition, few studies have explored the bandgap structure changes after incorporating hematite with Ti dopants, except that density function calculation results indicate a decrease of 0.2 eV of valence band edge in Ti-doped hematite [33]. We do not observe the existence of pseudobrookite, i.e. Fe2TiO5, or TiO2 in our samples, which functions to form heterojunction structure with α- Fe2O3, facilitating the separation of charge carriers [31,35], or pas- sivate surface trap states and reduce surface charge recombination in hematite [36]. The main reason for the enhanced photoactivity of Ti-doped hematite could be that Ti atoms can serve as dopants and increase the major carrier density in hematite, since one vacancy is formed with the doping of three Ti (IV) atoms [33]. The hematite phase could be well-preserved without

the appearance of co-ex- isting phase, even at high Ti doping percentage (up to 17%) [33]. Besides, the high temperature treatment (

33**800 °C for 10 min**) would facilitate **the** diffusion **of Ti**

atoms and further ensure a relatively uniform

3**distribution of Ti atoms in hematite**

[32]. 4. Conclusion In summary, an ion implantation technique was introduced to improve the PEC water oxidation performance of hematite in this study. After the post-annealing process, titanium plasma implanted β-FeOOH film was converted to titanium ion implanted α-Fe2O3 with lower charge transfer resistance and higher charge carrier density. Well-distributed Ti-doping increases charge carrier transport which simultaneously reduces the recombination of photogenerated charge carriers, therefore enhancing PEC water oxidation perfor- mance. Consequently, this work demonstrates the benefit of surface- engineered doping of hematite photoanodes using plasma ion im- plantation, along with a qualitative and quantitative understanding of impurity doping effects,

13**which can provide new insights into the development of** photo-responsive **materials for practical** applica- tions **in the emerging field of hydrogen technology**

. CRediT authorship contribution statement Y. P.

1**and H.-Y.H. contributed to the design concept**. Y. **P**

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1**and Q. R. performed the fabrication process and measurements. All authors discussed the results and commented on the manuscript. Declaration of Competing Interest**

There are no conflicts to declare.

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3410.1016/j.jallcom.2021.159376. **References**

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