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The influence of Ti doping on morphology and photoelectrochemical properties of hematite grown from aqueous solution for water splitting

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Abstract: Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a promising material for photoelectrochemical (PEC) water splitting. However, the poor conductivity and short hole diffusion length have limited its energy conversion efficiency. Nanorod structure could improve the transport of charge carriers and increase the reaction sites. Herein, we have investigated the influence of Ti doping on the morphology change and find that insufficient precursor concentration is the main reason for the morphology deviation from the optimized nanorod structure. The photoelectrochemical performance of the Ti-doped nanorod hematite was investigated and optimized. Analysis shows Ti plays a crucial role in improving both the bulk charge separation and surface charge transfer. We have also analyzed the limiting factor of the performance and the corresponding solution. Our systematic investigation indicates that the electron transport is still a limiting factor for the PEC performance of hematite. Further improvement can be obtained through replenishing the Ti source during the nanorod growth, and by subsequent nitrogen treatment.

Keywords: Photoelectrochemical water splitting; Hematite; Ti doping; Single crystal nanorod.

1. Introduction

Hematite ($\alpha\text{-Fe}_2\text{O}_3$) is a promising material for photoelectrochemical water splitting. It is earth abundant, chemically stable, and non-toxic. The narrow bandgap of 2.1 eV accounts for a theoretical solar to hydrogen (STH) efficiency of 15%.^[1] However, several drawbacks of hematite have posed great challenges for its application, such as lower flat-band potential, low absorption coefficient, slow oxygen evolution kinetics, poor conductivity, and short hole diffusion length.^[2] To overcome these limitations, enormous efforts have been made, including oxygen evolution **cocatalysts** loading to lower the kinetics barrier,^[3] doping to improve the electron conductivity,^[4] and nanostructure formation to increase the reaction surface area and to facilitate the hole diffusion.^[1a, 2]

One-dimensional nanostructures have the apparent merits of enhancing light absorption, promoting the charge carriers' transport, providing large reaction sites and better charge collection, which are very attractive for hematite and crucial for high solar conversion efficiency.^[1b, 5] A facile method for nanorod or nanowire structured hematite was first reported by Hagfeldt and co-workers,^[6] and then employed widely in many researches for photoelectrochemical water splitting.^[1a, 7] However, the synthesized nanorod morphology is mostly confined to pristine hematite. Besides the issue on hole diffusion, poor electron conductivity is also a limitation for hematite. To improve the conductivity, two main approaches can be employed: i) creating oxygen vacancy; ii) elemental doping. Li's group reported greatly enhanced performance of pristine hematite nanorod by thermal treatment in oxygen-deficient atmosphere compared to the one annealed in air.^[1a] The formation of oxygen vacancy was cited as the reason for the enhancement. Further investigation by other researchers showed that the photoelectrochemical water splitting performance was very sensitive to the oxygen partial pressure during annealing, which determines

the oxygen vacancy concentration.^[8] Thus, delicate control of the oxygen vacancy concentration becomes the key to obtain high performance. Meanwhile, other researchers tried elemental doping to improve the conductivity.^[9] Yang and coworkers introduced Sn-doping into the nanowires by dropping SnCl₄ ethanol solution onto the α -FeOOH film, then sintered in air at a high temperature to achieve Sn-doping.^[10] Similar strategy was also employed for Ti doping by dip coating or soaking with the Ti-source solution.^[11] However, the authors also pointed out that this kind of doping will form a disordered surface layer or surface states from unreacted species and/or uncompleted diffusion of dopant, which reduced the charge transfer efficiency from the hematite surface to the electrolyte.^[10-11] Other strategy, such as using TiO₂ underlayer, also showed performance enhancement.^[12] Researchers also used TiCN powder as the doping source and observed performance improvement.^[8b, 13] Summarizing all these attempts for doping hematite nanorod, an apparent strategy to simplify the materials processing is to add the dopants directly into the precursor and synthesize the hematite nanorod in one step. This was actually attempted, but it was found that the morphology have changed after Ti and Sn doping, which showed compact structure other than nanorods.^[14] It was reported that it was difficult to incorporate a sufficient amount of Ti ions in hematite through a hydrothermal method, because the doping source Ti in the solution decreased the pH value and makes it difficult to precipitate Fe³⁺.^[15] Fu et al. completed the incorporation of Ti ions and simultaneously retained the nanorod structure of hematite by decreasing the dopants to an extremely low level.^[15a] However, the photocurrent performance was also limited by the insufficient amount of Ti, which only had a photocurrent density of less than 0.8 mA/cm² under illumination of 100 mW/cm².^[15a] Thus, it is challenging to incorporate sufficient dopants and retain the nanorod structure by the hydrothermal method. It is also important to investigate the mechanism of the observed interesting morphology change from nanorod into

planar structure due to previously reported doping treatment and find a corresponding solution.^[14a, 14c, 16]

Driven by the curiosities, in this study, we have investigated the influence of Ti doping on the morphology change of hematite film from the view of ferric oxide nanorod growth mechanism. Nanorod structure was obtained by tuning the FeCl_3 concentration in the precursor. The photoelectrochemical performance of the nanorod Ti-doped hematite was then investigated and optimized. Moreover, the limitation in the performance of nanorod structured Ti-doped hematite was analyzed. Lessons generated were applied to improve the photoelectrochemical performance of hematite photoanode.

2. Material and methods

2.1 Preparation of hematite thin films

Ti-doped hematite nanorod thin films were fabricated on fluorine-doped tin oxide (FTO) coated glass substrates according to previous work with modification. All the procedures were carried out in ambient environment. A Teflon vial of 40 ml capacity was filled with 20 ml aqueous solution containing 1 M FeCl_3 , 1 M NaNO_3 and 20 μl 10 wt% TiCl_3 in 20-30% HCl solution. A piece of the FTO glass slide, cleaned before use, was back full covered and front half covered with a thermal tape, and then put into an oven preset at 95 °C for different reaction times (3 - 6 h) to prepare films with different thicknesses. Uniform yellow FeOOH nanorod thin films were grown on the FTO substrates. The obtained thin films were washed with deionized water and annealed in air at 700 °C for 20 minutes. For comparison, the influence of the Fe^{3+} precursor concentration on the morphology was investigated by tuning the Fe^{3+} concentration with other procedures kept the same. A two-step synthesis of nanorod Ti-doped hematite was similar to Ti-doped hematite

nanorod preparation, except for an intermediate addition of 20 μl TiCl_3 into the vial. In this two-step process, the first step follows the same procedure described above using a Teflon vial of 40 ml capacity filled with 20 ml aqueous solution containing 1 M FeCl_3 , 1 M NaNO_3 and 20 μl 10 wt% TiCl_3 in 20-30% HCl solution. The coated FTO glass was put into an oven preset at 95 $^{\circ}\text{C}$ for 3 h. After that, the vial was taken out and added with another 20 μl 10 wt% TiCl_3 in 20-30% HCl solution with stirring. The reaction was continued for another 2 h at 95 $^{\circ}\text{C}$. The obtained thin films were also washed with deionized water and annealed in air at 700 $^{\circ}\text{C}$ for 20 minutes. Post synthesis nitrogen treatment of the Ti-doped samples was carried out in a tube furnace at 500 $^{\circ}\text{C}$ for 2 h with N_2 flow rate at 50 sccm. The tube furnace was first vacuumed before the N_2 annealing. Pristine hematite nanorod thin films were annealed at 550 $^{\circ}\text{C}$ for 2h to achieve the best performance according to a previous work.¹ The synthesis parameters are summarized in Table S1.

2.2 Characterization

The morphologies and thickness of the hematite nanorod thin films were characterized using field emission scanning electron microscopy (FESEM, JEOL JSM-7600F). Crystallinity was identified by X-ray diffraction (XRD, Shimadzu 6000 X-ray diffractometer) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.154 \text{ nm}$). The chemical state of Ti was investigated by X-ray photoelectron spectroscopy (XPS, Omicron EA125). The binding energy was calibrated by C1s (284.6 eV). The selected area electron diffraction pattern and lattice structure were analyzed by a transmission electron microscope (TEM, JEOL JEM-2010F). Ti-dopant distribution was analyzed by energy-dispersive X-ray spectroscopy (EDS) elemental mapping equipped on a field emission scanning electron microscopy with transmission electron detector (FESEM, JEOL JSM-7600F). The light absorption efficiencies of pristine and Ti-doped hematite were obtained by measuring the reflectance and transmittance using UV-Vis-NIR spectrophotometer with an integrating sphere (Lambda 950,

Perkin-Elmer). Photocurrents were performed using a three electrode setup (PCI4/300™ potentiostat with PHE200™ software, Gamry Electronic Instruments, Inc.), with the hematite nanorod electrode as the working electrode, Pt mesh as the counter electrode and Ag/AgCl as the reference electrode. An AM 1.5G solar simulator (HAL-320, Asahi Spectra Co., Ltd.) with power intensity of $100 \text{ mW}\cdot\text{cm}^{-2}$ was used as the light source. The photocurrent measurement was performed with a mask (0.28 cm^2 exposed area) covered on the hematite thin film surface in 1 M NaOH aqueous (ph=13.6) solution with a scan rate of $30 \text{ mV}\cdot\text{s}^{-1}$. Electrochemical impedance spectra and Mott-Schottky plots were obtained using an AUTOLAB Potentiostat-Galvanostat (AUTOLAB PGSTAT302 N) at a fixed frequency of 1 kHz in 1 M NaOH solution.

3. Results and discussion

3.1 Effect of Ti doping on the morphology of pristine and Ti-doped hematite by hydrothermal reaction

Fig. 1 SEM images of (a) Pristine Nanorod hematite and (b) Ti-doped Planar hematite.

Morphologies of the hematite with and without Ti dopant are shown in Fig. 1. The morphology changes significantly with Ti dopant in the precursor, under the same synthesis procedure. The only difference is the addition of TiCl_3 for the purpose of Ti doping. The Pristine Nanorod hematite shows a clear nanorod structure, while the Ti-doped Planar hematite is of planar structure with some cracks. This means Ti affects the film growth process. This observation is also found in some previous reports.^[14] However, no investigation has been done to find out the reason and corresponding solutions.

Fig. 2 SEM images of (a) pristine hematite without any TiCl_3 in the precursor solution, (b) Ti-doped hematite with 20 μl TiCl_3 added in the precursor solution, and (c) Ti-doped hematite with 60 μl TiCl_3 added in the precursor solution.

Another feature observed is that the thickness of the grown film also changes with Ti doping. Under the same reaction time of 4h, the film without Ti doping can grow as thick as 500 nm (Fig.

2a), while the Ti-doped one with 20 μl TiCl_3 added in the precursor solution is only about 250 nm (Fig. 2b). It is therefore concluded that the presence of Ti lowers the film growth rate. Considering that the film porosity might also affect the measured film thickness, we compared two films with different Ti concentration (20 μl and 60 μl in the precursor), as shown in Fig. 2b and Fig. 2c. As seen, the morphologies are almost the same, which are composed of nano particles without nanorod structure. However, the film thickness is very different. With increasing Ti source concentration, the film thickness decreases.

Fig. 3 SEM images of Pristine Nanorod hematite grown in the solution for (a) 2 h, (b) 3 h, (c) 4 h; SEM images of Ti-doped Planar hematite grown in the solution for (d) 2 h, (e) 3 h, (f) 4 h. (g) Nanorod length and (h) diameter measured from the statistic results in SEM images.

In order to clarify what reason that causes such morphology change by Ti doping, SEM images of the nanorods grown in the solution (not on the FTO substrate) for different times are shown in Fig.

3. For pristine hematite without adding any Ti source, the length and diameter of the nanorod increase with reaction time. While for the one with TiCl_3 addition to the precursor, the length and diameter first increase and then decrease with time. It reflects that the nanorod cannot grow longer when TiCl_3 is present in the solution. In addition, in the presence of Ti in the precursor solution, there are much more precipitates in the solution than the one without Ti source. This implies that nucleation is easier to happen in the presence of TiCl_3 . This is possibly due to that TiCl_3 is easily oxidized into Ti^{4+} at heating condition and then hydrolyzed in an aqueous solution ($\text{TiCl}_4 + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{HCl}$), which provides more nucleation centres. In such condition, the Fe^{3+} will be exhausted faster and cannot support the continued growth. According to Hagfeldt and co-workers, nucleation takes place more easily onto a substrate than in solution due to the lower interfacial energy between the crystal and the substrate than that between the crystal and the solution.^[6] If the growth rate is controlled, epitaxial crystal growth is more likely to happen from these nuclei, and along the easy direction of crystallization. Single-crystalline nanorods perpendicular to the substrate will be obtained when the concentration of precursors is high.^[6] However, in the presence of TiCl_3 , a fast nucleation happens in the solution prior to the growth on the substrate. That explains why the high Ti concentration in the precursor solution has resulted in a thinner film thickness (Fig. 2b and 2c). On the other hand, the growth of nanorod in the solution is also limited in the presence of Ti, which is less than 600 nm in length even with longer reaction time. According to Hagfeldt et al.'s work, a high concentration of precursors, a low pH, and a high ionic strength is critical to grow nanorod.^[6] In the solution, ionic strength, which depends on NaNO_3 concentration, is kept the same. And the pH in the solution can only reduce due to the hydrolysis of Ti which

release HCl. Hence, based on our experimental observations and analysis, we deduce that Ti promotes a fast nucleation and exhausts the Fe^{3+} concentration, which cannot support a longer nanorod growth. If this analysis is true, it is reasonable to believe that increasing the FeCl_3 concentration in the precursor would promote the nanorod growth.

3.2 Effect of Fe^{3+} concentration on growth of single crystal Ti-doped hematite nanorod

Fig. 4 SEM images of Ti-doped Nanorod hematite with different FeCl_3 concentration.

Based on the above analysis, the effect of Fe^{3+} concentration on the morphology is investigated. The Fe^{3+} concentration in the precursor ranges from 0.15 M to 1.5 M and the morphology changes accordingly as shown in Fig. 4. For a low Fe^{3+} concentration (0.15 M), Ti-doped hematite shows a planar structure. With increasing concentration, nanostructure emerges. With Fe^{3+} concentration higher than 1 M, nanorods can be obtained. In addition, from the precipitation adhering onto Ti-doped hematite thin film surface the nanorod grows longer, from 100-200 nm to 600-700 nm with increasing the Fe^{3+} concentration from 0.15 M to 1 M (Fig. S1). Hence, the precursor concentration

is indeed a key factor to affect the morphology of Ti-doped hematite. It is noted that the pH value also changes with different FeCl_3 concentration. For 0.15 M FeCl_3 precursor solution, the pH is about 1.3, while for 1 M FeCl_3 the pH is about 0.6. Thus, pH may be another reason to affect the morphology. Considering this possibility, we did another experiment with 0.15 M FeCl_3 precursor and same amount of Ti, and adjusted the pH to about 0.6 (same as that of the 1 M FeCl_3). After 4 h reaction (up to 24 h), the solution was still very clear and nothing was grown on the FTO substrate. This indicates that nanorod can hardly grow in such low pH solution if the FeCl_3 precursor concentration is not high enough.

Fig. 5 X-ray photoelectron spectra of (a) C 1s, (b) Fe 2p, (c) Ti 2p and (d) O 1s core level of pristine and Ti-doped nanorod hematite. (e) TEM images with the inset displaying the corresponding SAED pattern (top left), higher resolution image (top-right) corresponding to the

rectangle area in the top left Fig., and EDS mapping (bottom) of Ti-doped hematite nanorod. (f) X-ray diffraction patterns of nanorod-structured pristine and Ti-doped nanorod hematite.

The incorporation of Ti dopants into the hematite nanorod structure is analyzed by X-ray photoelectron spectroscopy (XPS). The binding energy of C 1s at 284.6 eV is used as reference to correct the binding energies (Fig. 5a). The Fe 2p_{3/2} core level of pristine and Ti-doped nanorod hematite are shown in Fig. 5b. The same peaks at 724.1 and 710.6 eV for both pristine and Ti-doped hematite confirm the typical Fe³⁺ ionic state, which also proves that Ti doping has not changed the Fe³⁺ ionic state. For Ti-doped sample, the Ti 2p_{3/2} line shows distinct peaks at 458.1 and 463.8 eV, confirming the presence of Ti⁴⁺ ions in the Ti-doped nanorod hematite,^[4c, 12] while for the pristine sample no Ti within the detection limit is shown from the surface (Fig. 5c). The calculated Ti/Fe atomic ratio is about 2:25 from XPS results. It is also found that Ti doping causes a slight shift in the binding energy of O 1s, which also proves the doping effect (Fig. 5d). The nanorod structured Ti-doped hematite was further analyzed by transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) mapping (Fig. 5e). The TEM images of one individual nanorod confirm the SEM results that the prepared thin film is composed of nanorods. The clear spots in the selected area electron diffraction (SAED) pattern and higher resolution image show that the Ti-doped nanorod hematite is single crystalline growing along the [110] direction. The EDS elemental mapping shows that Ti has been successfully incorporated into the hematite nanorod throughout the whole nanorod (from root to tip). The XRD shows that the prepared nanorod-structured Ti-doped hematite have the same crystal structure with the pristine hematite (Fig. 5f), and both indicate a preferential orientation of the nanorod growing along the [110] direction, which proves the observed SAED pattern. Two weak peaks near 34 degree and 54 degree belonging to hematite phase are found for the Ti-doped sample, while there are no obvious peaks

in the same locations for the pristine sample. It could be due to a slightly favorable texture of the (104) and (116) planes of the doped sample.

3.3 Photoelectrochemical performance of single crystal Ti-doped hematite nanorod thin film

Fig. 6 Photocurrent densities at 0.23 V vs. Ag/AgCl (1.23 V vs. RHE) of Ti-doped hematite with different (a) reaction time, (b) content of the doping source TiCl₃ in the precursor solution. (c) Photocurrent density of nanorod structure Ti-doped hematite, planar Ti-doped hematite and nanorod structured pristine hematite.

After the nanorod structure has been successfully synthesized, doping concentration and reaction time are optimized. The best performance is achieved at the condition of 4 h reaction using 20 μl TiCl_3 in the precursor solution (Fig. 6a and b). Fig. 6c shows the photocurrent of nanorod structured Ti-doped hematite is greatly enhanced compared with pristine nanorod hematite, which is mainly attributed to the improved electron carrier density and better conductivity due to the incorporation of Ti dopants as confirmed by the XPS and TEM (Fig. 5). It is noted that the photocurrent of the pristine sample was negligible. That is possibly due to the intrinsically poor electron conductivity of hematite, coupled with the fact that the film was too thick for the electron to travel such a long distance. Besides, the nanorod structure in the Ti-doped hematite is also a contributing factor due to increased reaction sites and improved hole diffusion. In many reports, nanostructuring has significant improvement compared with planar structure, typically 2 times enhancement or more.^[7a, 17] However, in this study, the enhancement is not as significant. To understand the reasons, front (electrolyte-hematite side) and back (FTO-hematite side) illumination photocurrents were compared next for the nanorod structured Ti-doped hematite with different reaction times. For front-side illumination, most of the photo-excited carriers are generated at the hematite-electrolyte interface. Thus, the photo-generated electron travels a relatively long distance to the FTO, while the hole travels a relatively short distance to the electrolyte. On the contrary, for the back side illumination, most of the photo-excited carriers generate at the FTO-hematite interface. Thus, the electron travels a relatively short distance to the FTO, while the hole travels a relatively long distance to the electrolyte. Based on comparison of the photocurrent density of the two illumination modes, the relative transport property of electron and hole can be comprehended.^[18]

Fig. 7 Photocurrent density of Ti-doped Nanorod hematite (1 M, 3-6 h) with different reaction time illuminated from front (sample side) and back side (FTO side).

Fig. 7 shows the front and back illumination photocurrents of nanorod structured Ti-doped hematite with different reaction times, which represent different thicknesses from 240 to 630 nm (Fig. S2). As shown, for thin film (less than 400 nm corresponding to 3h and 4h samples) the front illumination photocurrent is larger than that of back illumination photocurrent. However, for thicker film (larger than 500 nm corresponding to 5h and 6h samples), the front illumination photocurrent is smaller than that of back illumination photocurrent. This indicates that for thicker film, the electron transport is a limit factor for the PEC performance. This could possibly be caused

by decreasing Ti doping source concentration with reaction time, making it Ti-deficient for effective doping in the thick films.

Fig. 8 Front (electrolyte/hematite side) and back (FTO/hematite side) side illumination photocurrents of the one-step synthesized Ti-doped nanorod hematite and the two-step synthesized Ti-doped nanorod hematite.

In order to verify this hypothesis, a two-step synthesis of nanorod Ti-doped hematite is employed. After 3 h reaction, the vial was taken out and added with 20 μl TiCl_3 . The reaction was then continued for another 2 h. The photocurrents of the two-step synthesized nanorod hematite is shown in Fig. 8. For comparison, the one-step synthesized nanorod Ti-doped hematite for 5 h is also given without adding Ti source during the reaction, which has almost the same thickness. For the one-step synthesized nanorod Ti-doped hematite, the front side illumination photocurrent is lower than that under back illumination, which indicates the electron transport is the limiting

factor. However, for the two-step synthesized Ti-doped nanorod hematite, the front side illumination photocurrent is larger than that under the back side illumination, which indicates a better electron conductivity with two-step doping. The photocurrent is better than that of the one-step synthesized Ti-doped nanorod hematite, which benefits from the improved electron conductivity (Fig. S3) by better Ti doping (Fig. S4).

3.4 The role of Ti on performance of the crystalline Ti-doped nanorod hematite

Fig. 9 (a) SEM images, (b) light absorption efficiencies, (c) charge separation efficiencies and (d) interfacial charge injection efficiencies of Pristine and Ti-doped Nanorod hematite thin films with comparable thickness.

The above analysis shows that the Ti doping plays an important role in improving the performance of nanorod hematite. To make a comprehensive understanding of the role of Ti, we select nanorod structured hematite with and without Ti doping with the comparable thickness of around 500 nm (Fig. 9a) for comparison. The selected two samples have almost the same structure and thickness, thus, the light absorption efficiencies of both the two samples are very similar (Fig. 9b). The theoretical photocurrents of pristine and Ti-doped nanorod hematite calculated from the light absorption under 1 sun illumination (AM 1.5G data) both are 10.3 mA/cm². The electron and hole separation efficiency and interfacial hole injection efficiency can be estimated as follows. The water oxidation photocurrent is expressed by equation (1):^[19]

$$J_{H_2O} = J_0 \times \eta_{abs} \times \eta_{sep} \times \eta_{inj} \quad (1)$$

where J_{H_2O} is the water splitting photocurrent, J_0 is the theoretical solar photocurrent (12.6 mA/cm² for hematite), η_{abs} is the light absorption efficiency, η_{sep} is the charge separation efficiency, and η_{inj} is the interfacial hole injection efficiency to oxidize water. When using a hole scavenger Na₂SO₃, the interfacial hole injection efficiency can be assumed to be 100% ($\eta_{inj}=1$) due to the fast oxidation of Na₂SO₃.^[19] The hole scavenger Na₂SO₃ oxidation photocurrent can be determined by equation (2):^[19]

$$J_{Na_2SO_3} = J_0 \times \eta_{abs} \times \eta_{sep} = J_{abs} \times \eta_{sep} \quad (2)$$

where $J_{Na_2SO_3}$ is the oxidation photocurrent of Na₂SO₃, J_{abs} is the maximum photocurrent of hematite based on its light absorption efficiency. From equation (1) and (2), we can obtain $\eta_{sep}=J_{Na_2SO_3}/J_{abs}$ and $\eta_{inj}=J_{H_2O}/J_{Na_2SO_3}$. The charge separation efficiency of pristine nanorod hematite is only 1%, while that of Ti-doped nanorod hematite is about 18% at 0.6 V vs. Ag/Ag Cl

(Fig. 9c). The interfacial hole injection efficiency of pristine nanorod hematite is 12%, and that of Ti-doped nanorod hematite is about 85% at 0.6 V vs. Ag/Ag Cl (Fig. 9d). It is concluded that Ti doping plays a crucial role in both the charge separation and charge injection.

Fig. 10 (a) Mott-Schottky plots measured at 1000 Hz of pristine and Ti-doped nanorod hematite thin films with comparable thickness. (b) Electrochemical impedance spectroscopy (EIS) of pristine and Ti-doped nanorod hematite thin films with comparable thickness measured at 0.23 V vs. Ag/AgCl under 1 sun illumination. Inset is the equivalent circuit used to simulate the EIS data. (c) C_{ss} for pristine and Ti doped naorod hematite (d) Cyclic voltammetry scan in the dark after

holding the electrode at the potential of 0.5 V vs. Ag/AgCl for 120 seconds under 1 sun illumination of pristine and Ti-doped nanorod hematite thin films with comparable thickness.

Mott-Schottky plots of pristine and Ti-doped nanorod hematite were measured to investigate the carrier density (Fig. 10a). The positive Mott-Schottky slopes demonstrate electrons as the majority carriers. The electron density can be estimated by equation (3):^[20]

$$N_d = (2 / e_0 \varepsilon \varepsilon_0 A^2) \left[d(1 / C^2) / dV \right]^{-1} \quad (3)$$

where e_0 is the electron charge (1.60×10^{-19} C), ε is the dielectric constant of pristine hematite (80),^[21] ε_0 is the permittivity of vacuum (8.85×10^{-12} F·m⁻¹), A is area of the electrode, N_d is the carrier density and V is the applied potential, C is the surface capacitance. The carrier densities of pristine and Ti-doped nanorod hematite were calculated to be 2.1×10^{19} cm⁻³ and 3.4×10^{21} cm⁻³ respectively. It should be noted that our samples are in the nanorod form, the carrier density calculated using Equation 3, which is for a planar film, may not represent the actual density value. Therefore, we only use this equation to compare the carrier density among the nanorod samples. Such comparison can help us understand the carrier density change caused by Ti doping. The carrier density of Ti-doped nanorod hematite is 1 order of magnitude higher than the pristine one, assuming that the dielectric constant is the same. However, it was reported that doped hematite has a higher dielectric constant.^[22] Therefore the actual carrier density enhancement may be less.

Ti doping greatly enhances the carrier density, which improves the electron conductivity and results in a higher charge separation efficiency in the bulk. EIS was employed to analyze the surface hole injection. Fig. 10b shows the EIS of pristine and Ti-doped nanorod hematite. According to previous reported work, on hematite surface it is likely that water is oxidized from

surface trapped holes which are first trapped by the surface states other than the valence band holes.^[23] Here, we employ the same equivalent circuit reported in previous work to analyze the EIS data. In the equivalent circuit (inset in Fig. 10b), R_s is total resistance from external circuit; R_{trap} is the resistance of the surface states trapping holes; C_{ss} is the capacitance from the surface states; R_{ss} is the surface charge transfer resistance. It shows that the surface charge transfer resistance of Ti-doped nanorod hematite is only about 96 Ω , while that of pristine nanorod hematite is $5.20 \times 10^5 \Omega$. The difference is also reflected on the capacitance of the surface states (Fig. 10c). Pristine hematite has a lower charging potential than Ti doped sample, which means pristine hematite should have a lower onset potential if other factors are kept the same. However, compared with the pristine hematite, the Ti doped sample has a much larger surface state capacitance, which means more surface states have participated in the surface reaction. Therefore, although the pristine hematite has the advantage of a better onset potential, its photocurrent is lower than the doped sample. It indicates that Ti-doped hematite forms more surface states which have increased the charging and discharging on the surface and facilitates the charge transfer process for water oxidation. To further prove this, cyclic voltammetry scan in the dark was conducted after holding the hematite electrodes at the potential of 0.5 V vs. Ag/AgCl for 120 seconds under 1 sun illumination. Holding the electrode at a high potential under illumination will result in the charging of the surface states. Thus, cyclic voltammetry after turning off the illumination will cause reduction of those charged surface states and the surface states can be measured. As shown in Fig. 10d, no specific reduction peaks can be recognized except a marginal broad peak around -0.3 V vs. Ag/AgCl. In contrast, Ti-doped hematite shows a very obvious peak at about 0 V vs. Ag/AgCl corresponding to a specific active surface state, which nicely explains that the higher surface state

capacitance and much better charge injection efficiency. Hence, Ti plays an important role in both bulk charge separation and surface charge transfer.

3.5 Performance limitation of crystalline Ti-doped nanorod hematite

Fig. 11 (a) Photocurrent of the two-step synthesized nanorod Ti-doped hematite (green line), planar structured Ti-doped hematite (pink line) post treated in N₂ at 500 °C for 2h, and photocurrent of pristine nanorod hematite (red line) treated in N₂ at 550 °C for 2h to achieve the best performance according to a previous work.¹ Dark currents are shown in dashed lines. (b) Stability test of N₂ treated Ti-doped nanorod hematite at 0.23 V under 1 sun illumination.

In this study, the optimized photocurrent of crystalline Ti-doped hematite reaches about 2 mA/cm². It is still quite lower than the theoretical value (10.3 mA/cm²), which is mainly limited by the charge separation (less than 20%). It is supposed that the low charge separation comes from that the annealing temperature is not high enough for better doping effect, which can be proven from the fact that photocurrent correlates with the heating temperature (Fig. S5). However, the annealing temperature is limited by the FTO glass substrate, so we could not explore annealing at a higher temperature in the current study. In order to further improve the performance, oxygen vacancy was

introduced by annealing in nitrogen flow gas. Fig. 11a shows the photocurrent of N₂ treated Ti-doped hematite nanorod thin film. The nanorod structured Ti-doped hematite after nitrogen treatment shows enhancement with photocurrent at 0.6 V vs. Ag/AgCl close to 3 mA/cm². The efficiencies of N₂ treated Ti-doped hematite nanorod are given in Table S2. The charge separation efficiency is 31% (calculated based on the photocurrent with hole scavenger) at 0.6 V vs. Ag/AgCl, which has increased by 72% compared with the one without N₂ treatment (18%). Such a drastic improvement is believed to have benefited from improved electron conductivity due to the formation of oxygen vacancies after the nitrogen annealing, which can be proved by the Mott-Schottky plots (Fig. S6). This also proves our reasoning that electron transport is still a limit factor for Ti-doped hematite (31% even after N₂ treatment). However, the separation is still low in this case, because the theoretical photocurrent J_{abs} is very high due the good light absorption by the nanorod structure. Similar high performance has been achieved by annealing pristine nanorod FeOOH in an oxygen-deficient atmosphere.[1] However, we find in our experiment that for pristine hematite the oxygen content needs to be controlled very strictly to obtain suitable oxygen vacancy towards better electron conductivity for high performance. We also have repeated the result in our lab and the nanorod structured pristine hematite annealed in nitrogen atmosphere, by contrast, it only showed a maximum photocurrent of 0.5 mA/cm². However, with Ti-doping, we can easily achieve a similar high performance by a post annealing treatment of the synthesized Ti-doped nanorod hematite in nitrogen atmosphere using our system (Fig. 11a green line). Some representative photocurrents of hematite photoanodes reported by others are listed in Table S3. Our result is comparative with the reported work. Our results indicate that Ti-doping plays a key role in improving the electron conductivity of the nanorod-structured hematite through improved electron conductivity. In order to understand the contribution by the nanorod structure to the

performance enhancement, the planar structured Ti-doped hematite after the same nitrogen treatment was also measured, with the maximum photocurrent at around 1.7 mA/cm². This is a clear indication that nanorod structure contributes greatly in the photocurrent improvement. Combining all the above results, it is clear that that electron transport is a key limiting factor behind the photoelectrochemical performance of hematite nanorod structures. Ti-doping is critical in improving the electron conductivity of nanorod-structured hematite under nitrogen treatment. Hence, nanostructure formation and Ti doping are two effective means to achieve high performance hematite photoanode. Fig. 11b shows the stability of N₂ treated Ti-doped nanorod hematite, which indicates that the oxygen vacancy introduced by N₂ treatment is stable during the water oxidation.

4. Conclusions

Ti doping changes the morphology of pristine hematite from nanorod to planar structure. The reasons for such a change are that 1) Ti in the solution promotes fast nucleation of hematite, and 2) the Fe³⁺ concentration is reduced quickly, making its concentration too low to support the nanorod growth. With the root causes identified, single crystal nanorod Ti-doped hematite is successfully prepared by tuning the FeCl₃ concentration in the precursor. Ti is successfully doped into the hematite as evidenced by XPS and EDS mapping. The photoelectrochemical performance of the nanorod Ti-doped hematite is enhanced compared with the planar structured Ti-doped hematite. Front and back photocurrent comparison indicates that, the electron transport is a limiting factor for thicker films. The photocurrent is further improved by a two-step synthesis with intermediate addition of Ti source during the reaction. Ti greatly enhances the bulk charge

separation and surface charge transfer by increasing the carrier density and form active surface states. Post-synthesis nitrogen treatment has further enhanced the photocurrent density to ~ 3 mA/cm² at 0.6 V vs. Ag/AgCl. Nanostructure and Ti doping are identified as two key actions towards high PEC performance using hematite photoanode. The current study provides insights into the performance of hematite nanostructures, as well as guidelines for doping of nanostructured semiconductor thin films using a simple solution processing technique.

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