The influence of the hydrothermal temperature and time on morphology and photoelectrochemical response of α -Fe₂O₃ photoanode

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ABSTRACT:

By controlling the aging temperature and time, α -Fe₂O₃ photoanodes with different morphology are successfully prepared, such as nanorod and nanocolumn. High-aligned α -Fe₂O₃ nanorods photoanodes were prepared by hydrothermal method under lower aging temperature and medium aging time without Ostwald bending to obtain the optimal photoanode for photoelectrochemical water oxidation under solar light. The morphology, optical properties, photoelectrochemical response and charge transfer of the α -Fe₂O₃ photoanodes were investigated by X-Ray diffraction (XRD), UV-vis absorbance spectroscopy, scanning electron microscopy (SEM), Mott–Schottky (MS) and electrochemical impedance spectroscopy (EIS). The optimal α -Fe₂O₃ nanorods photoanode with 100 nm in diameter and 300 nm in thickness could be obtained under 95 °C for 5 h, which have the optimal photocurrent density up to 0.54 mA cm⁻² at 1.23 V (vs. RHE.) and 0.12 V negative shift in the onset potential of photocurrent compared with nanocolumns photoanodes. As revealed by EIS analysis, the enhanced photoelectrochemical response is mainly attributed to the decreased resistance of charge transfer inside the nanorods electrode and across the interface between electrode and electrolyte. This work provide an in-depth understanding of the relationship between hydrothermal synthesis process, morphology, crystalline structure and photoelectrochemical performance of α -Fe₂O₃ photoanode via systematically studied the photoanode prepared by hydrothermal method.

Keywords: α -Fe₂O₃ photoanode; morphology; photoelectrochemical response; hydrothermal process

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1. Introduction

With the continuously increasing energy demand, photoelectrochemical (PEC) approach was studied as one of the most promising technology for solar energy conversion. Hematite ($\alpha\text{-Fe}_2\text{O}_3$) has been extensively investigated as one of the best candidates for photoelectrochemical electrode due to its favourable band gap ($E_g=1.9\sim 2.2$ eV), excellent chemical stability in aqueous solution, abundance in the earth, and low cost [1-5]. However, there are also significant challenges associated with its application to solar energy conversion, including low absorption coefficient [6,7], poor carrier mobilities [8], and short hole diffusion lengths (2-20 nm) [9,10]. These reported results of photocurrent for hematite are notoriously lower than the theoretical value 12 mA cm^{-2} [4]. Since Hardee and Bard first turned to iron oxide as a material for water photolysis in 1976 [11], researchers have made many fruitful strategies to improve the efficiency of hematite photoanode including size- and morphology-controlling [12,13], metal oxide heterostructuring [14-16], doping [17-22], quantum dot sensitization [23], plasmonic metal nanoparticle attachment [24], and co-catalyst coupling [25-27]. Electronic or optical properties of hematite are strongly dependent on their sizes or morphologies, which have been made primarily to reduce photogenerated carrier recombination with nanostructure. Nanostructured $\alpha\text{-Fe}_2\text{O}_3$ materials have been synthesized by numerous approaches to achieve one-dimensional (1D) (such as nanorods, nanowires, and nanotubes), two-dimensional (2D), and three-dimensional (3D) nanostructures [28]. The main approaches include spray pyrolysis [29-31], atmospheric pressure chemical vapor deposition (APCVD) [12,17,25], atomic layer deposition (ALD) [32], DC magnetron sputtering [33], colloidal solution assembly [13,34], electrochemical deposition [21], anodization [35,36], and hydrothermal methods [2,37-39]. Among these methods, hydrothermal synthesis has the advantages of facile and cost-effective to synthesize high performance $\alpha\text{-Fe}_2\text{O}_3$ nanostructure photoanodes. However, most of the previous works focused on preparation modified hematite photoanodes basing on hydrothermal synthesized bare hematite, such as $\text{Fe}_2\text{O}_3/\text{WO}_3$ [40], $\text{Fe}_2\text{O}_3/\text{ZnO}$ [16], $\text{Sn-Fe}_2\text{O}_3$ [41], $\text{P-Fe}_2\text{O}_3$ [22], $\text{Sn-Fe}_2\text{O}_3$ [42], phosphate- Fe_2O_3 [43], $\text{Ti-Fe}_2\text{O}_3/\text{NiFeO}_x$ [44], $\text{Ti-Fe}_2\text{O}_3/\text{NiO}/\alpha\text{-Ni(OH)}_2$ [45], $\text{Pt-Fe}_2\text{O}_3/\text{Co-Pi}$ [46], $\text{Au/Zr-Fe}_2\text{O}_3/\text{Au}$ [47]. Only few works were aimed at bare hematite, Ferraz et al. [37] described the influence of the thermal treatment on the fundamental properties of the vertical oriented iron oxide nanorods, De Carvalho et al. [48] reported an oriented hematite undoped photanode synthesized by

single chemical route step at low temperature and with a short reaction time, and Li et al. [49] studied the influence of the synthesis temperature on morphology and growth mechanism of α -Fe₂O₃ nanorods (NRs) and 3D nanospheres. In this paper, we have prepared samples by hydrothermal method under different aging temperature and time to systematically investigate the influence of the hydrothermal process on the morphology, optical properties, photoelectrochemical activity and charge transfer of the α -Fe₂O₃ photoanode.

2. Experimental

2.1. Fabrication of α -Fe₂O₃ photoanodes

α -Fe₂O₃ films were prepared on F-doped SnO₂ glass (FTO) by hydrothermal method as reported by Vayssieres et al. [50] followed by annealing treatment. Initially, the FTO substrates were successively cleaned in an ultrasonic bath with detergent, deionized water, acetone, and ethanol for 20 min in sequence, and then dried with nitrogen gas flow. Secondly, 15 ml aqueous solution including 0.61 g FeCl₃ and 1.27 g NaNO₃ was transferred into a Teflon-lined stainless steel autoclave with a capacity of 80 mL and 3 pieces of FTO substrates (1×4 cm²) were declining placed at an angle of 75° and the conductive side facing down. The autoclave was sealed and then heated at 95 °C, 125 °C and 155 °C for 3 h, 4 h, 5 h and 6 h (denoted later as temperature-time, i.e., 95-3, 125-5) to grow β -FeOOH films. Then the as-synthesized β -FeOOH was successively annealed at 550 °C for 2 h and 750 °C for 10 min to convert to hematite.

2.2. Characterizations

The fabricated films were characterized by Rigaku D powder X-ray diffraction (max 2500PC) with CuK_α radiation (λ =0.154059 nm) at 40 kV and 150 mA. The UV-vis absorbance spectroscopy (Shimadzu, UV 2450) was used to probe the optical properties. The surface morphology and thickness of the samples were characterized by scanning electron microscopy (JEOL, JSM-6360LA, 20 kV).

2.3. PEC performance measurements

The PEC properties of the fabricated samples were investigated using a standard three-electrode electrochemical workstation (CHI 760E) in 1 M NaOH (pH=13.6) electrolyte under simulated solar light irradiation (AM 1.5 global, 1 sun (100 mW cm⁻²)). The working, counter and reference electrodes were the α -Fe₂O₃ photoanode, a platinum foil and Ag/AgCl (sat. KCl, E=0.1976V vs.

NHE.), respectively. The α -Fe₂O₃ photoanodes were masked by epoxy resin with a 0.38 cm² square hole to explore the PEC performance. The photocurrent was measured by linear sweep voltammetry from -0.6 to 0.7 V (vs. Ag/AgCl) with a scan rate of 0.03 V s⁻¹. The incident photo-to-current efficiency (IPCE) was measured under the same 300W Xe lamp equipped with a monochromator under potential of 0.23 V (vs. Ag/AgCl). The Mott–Schottky (MS) and Electrochemical impedance spectroscopy (EIS) were carried out employing the same electrochemical device except that a VersaSTAT 3 potentiostat was used. The MS plots were measured in the dark and under light illumination at 1 kHz. The EIS measurements were performed at 0.23 V (vs. Ag/AgCl) with the frequency range being adjusted between 100 kHz to 0.1 Hz at amplitude frequency 10 mV under light irradiation. The program Zsimpwin was used to fit the obtained data to the corresponding equivalent circuit model.

3. Results and discussion

3.1. Morphology Characterization of α -Fe₂O₃ photoanodes

In order to confirm the influence of aging temperature and time on the α -Fe₂O₃ photoanodes morphology, the top-view and cross-sectional SEM images associated with XRD are carried out. XRD patterns of the fabricated films can be indexed to the characteristic peaks of α -Fe₂O₃ (JCPDS NO:33-0664) (Fig. 3a). As seen in Fig. 1, Fig. S1 and Fig. 2, at 95 °C, all the α -Fe₂O₃ photoanodes are vertically grown on FTO substrate with the similar morphology as nanorods arrays with 100 nm in diameter and 300 nm in length. At the beginning of hydrothermal synthesis, β -FeOOH nuclei appears on the entire FTO substrate and epitaxial crystal growth takes place from these nuclei perpendicular to FTO substrate, and then the β -FeOOH single-crystal densification laterally with the aging time increased from 3 h to 6 h. At 125 °C, all the α -Fe₂O₃ photoanodes have the same length of 450 nm, the 125-3 photoanodes have clear nanorods morphology with 80 nm in diameter, the 125-4 and 125-5 photoanodes have ambiguous nanorods morphology with limited tilt angles, and the 125-6 photoanodes have the adjoining nanorods adhered together to form nanocolumn with non uniform nanoparticles attached to the surface. With higher temperature of 125 °C, more and smaller β -FeOOH nuclei appears on the entire FTO substrate and epitaxial crystal growth takes place from these nuclei with limited tilt angles, and the crystal densification laterally with the aging time increased. As the aging time increased from 3 h to 5 h, the β -FeOOH single-crystals progressively adjoin together and

result in ambiguous nanorods morphology. And as the aging time increased to 6 h, the β -FeOOH single-crystals too tight to increase, and new β -FeOOH nuclei appears on the surface of the 125-6 sample. At 155 °C, all the α -Fe₂O₃ photoanodes have the first layer film with the same length of 1000 nm and different density. As the aging time increased, the first layer film become tightness enough and the second layer film begin to form. β -FeOOH nuclei appears on the entire FTO substrate and epitaxial crystal growth takes place from these nuclei with larger tilt degree, then the single-crystals adjoin together easily to form large nanocolumn particles attached to the surface.

To better illustrate the formation mechanism of the samples morphology, the schematic model for the growth process of β -FeOOH and α -Fe₂O₃ film was shown in Fig. 4. We proposed three major steps in the formation of final products as follows: (i) fast nucleation process; (ii) Ostwald ripening; (iii) annealing for converting. With low temperature of 95 °C, and high concentration of precursors, β -FeOOH nuclei appears on the entire FTO substrate and epitaxial crystal growth takes place from these nuclei along the easy direction of crystallization, and then the β -FeOOH single-crystal alternate densification laterally and thicken longitudinally with the aging time increasing. Then the as-synthesized β -FeOOH was annealed at 550 °C for 2 h and 750 °C for 10 min to convert to nanorods hematite, which highly oriented in the [110] direction on the substrate with strong (110) diffraction peak at $2\theta=35.8^\circ$ (Fig. 3 (a)). At higher temperature of 125 °C, it undergo a similar, but faster, process of more and smaller β -FeOOH nuclei and single-crystal formation comparing with low temperature. At the same time, the single-crystal with limited tilt angles caused by Ostwald bending assembles with each other by side-to-side and end-to-end. Under followed annealing, as the aging time less than or equal to 5 h, the relatively loose single-crystal bundles convert to nanorod hematite, which oriented in the [110] direction on the substrate with strong (110) diffraction peak at $2\theta=35.8^\circ$ and two minor diffraction peaks of (104) and (116) at $2\theta=33^\circ$ and $2\theta=54^\circ$ (Fig. 3 (a)). While as the aging time increased to 6 h, the compact single-crystal bundles convert to nanocolumn hematite, which has three strong diffraction peaks of (104), (110) and (116) (Fig. 3 (a)). As the temperature increased to 155 °C, more nuclei and larger tilt degree single-crystal is formed with stronger thermodynamic force in a short time such as 3 h. Then the randomly grown single-crystal adjoin to each other to tend to form nanocolumn. After annealing, the as-synthesized β -FeOOH convert to adjoining nanocolumns and scattering nanocolumns, which has three strong diffraction

peaks of (104), (110) and (116) similar to 125-6 sample (Fig. 3 (a)). The aging temperature and time play vital roles in determining the morphology and size of the α -Fe₂O₃ nanostructures by Ostwald bending. At low temperature, such as 95 °C, epitaxial crystal growth takes place from the nuclei perpendicular to FTO substrate without Ostwald bending, and then the 95 specimens grow along a specific direction with a main peak of (110). At high temperature, such as 155 °C, epitaxial crystal growth takes place from the nuclei with larger tilt degree according to Ostwald bending, and then the 155 specimens undergo isotropic growth which have the same three main peaks of α -Fe₂O₃ (JCPDS NO:33-0664) as (104), (110) and (116).

UV-vis spectra of α -Fe₂O₃ photoanodes are shown in Fig. 3b, c and d. The UV-Vis absorbance of the α -Fe₂O₃ photoanodes have a clear edge around 600 nm, which corresponds to the band gap of the electrodes. The $(\alpha h\nu)^{1/2}$ - $h\nu$ plot show an indirect optical band gap of 2.0-2.1 eV similarly for all hematite photoanodes (Fig. S2), which are in accordance with that of typical α -Fe₂O₃ photoanode films [51]. Apparently, the notable higher absorbance was found for the 125-6, 155-4, 155-5 and 155-6 in the range of 600 to 800 nm. As shown in Fig. 1, Fig. 2 and Fig. 3a, it can be found that the above-mentioned samples (155-4, 155-5, and 155-6) have isotropic growth and nanocolumn shape with 0.5-1 μ m in diameter, and the sample 125-6 have the adjoining nanocolumns adhered together with large grain size appearance. According to Mie scattering theory [52], the higher absorbance of the above-mentioned samples were due to the dramatically scattered incident light as the nanosphere size of the samples is comparable to the wavelength of the light.

3.2. Photoelectrochemical properties

To investigate the photoelectric performance of the α -Fe₂O₃ photoanodes prepared from different aging temperature and time, the photocurrent response under simulated solar light irradiation has been measured with a three-electrode photoelectrochemical workstation. Fig. 5 shows the photocurrent density-potential curves of different α -Fe₂O₃ photoanodes. In this paper, the photocurrent density is read off at 1.23 V (vs. RHE.), which is the standard reversible potential for water oxidation. At 95 °C (Fig. 5a, Fig. S3a), the 95-5 α -Fe₂O₃ photoanode shows the highest photocurrent density of 0.54 mA cm⁻², while it has the lowest photocurrent density of 0.39 mA cm⁻² for 95-3 α -Fe₂O₃ photoanode. The difference of photocurrent density may be attributed to the stronger light absorption for the greater thickness of the α -Fe₂O₃ films, which is in consonance with

UV-vis absorbance spectra of the electrodes (Fig. 3b). At 125 °C (Fig. 5b, Fig. S3b), the 125-3 α -Fe₂O₃ photoanode of nanorods with 450-nm-thickness shows the highest photocurrent density of 0.53 mA cm⁻², and the others electrodes have notable lower photocurrent density. The nanorod-like morphology of 95 and 125-3 photoanodes have a desired orientation for charge transport because the conductivity of this basal plane (110) shows four orders higher than that of orthogonal plane, improving the photo-oxidation kinetics [3,53,54]. Combining SEM (Fig. 1, Fig. 2) and XRD (Fig. 3a), the low photocurrent density of the others photoanode can be attributed to the growth of (104) and (116) planes. At 155 °C (Fig. 5c, Fig. S3c), 155-3 α -Fe₂O₃ photoanode shows the highest photocurrent density of 0.23 mA cm⁻², and the others are 0.12, 0.05, 0.02 mA cm⁻², respectively. The isotropic growth **nanocolumns** hinder the charge diffusion and increase excess combination loss, and thus depress the photocurrent density of α -Fe₂O₃ photoanodes. According to Li et al. [47], the nanospheres α -Fe₂O₃ annealed from 160 °C with 500 nm in diameter have the highest photocurrent response around 0.55 mA cm⁻² at 1.23 V (vs. RHE.), while in our paper, nanorod photoanodes annealed from 95 °C with 100 nm in diameter and 300 nm in thickness have the highest photocurrent response of 0.54 mA cm⁻².

To clarify the origin of the different photocurrent response and electron transport mechanism, the MS has been measured and analyzed. Fig. 6a and b show the flat-band potential and donor density of the photoanodes in the dark and under light irradiation, which based on Mott-Schottky equation [55,56]:

$$\frac{1}{C^2} = \frac{2}{\epsilon\epsilon_0 q N_D A^2} (E - E_{fb} - k_B T/q) \quad (1)$$

where C is the capacitance of the space charge layer, ϵ is the dielectric constant of the semiconductor, ϵ_0 is the vacuum permittivity, q is the elementary charge, N_D is the donor density, A is the actual area of the electrode exposed to the electrolyte, E is the applied potential, E_{fb} is the flat-band potential, k_B is the Boltzmann constant, and T is the temperature. According to the equation, the donor density and flat-band potential can be deduced from the slope and intercept of the Mott-Schottky plots (Fig. S4), respectively. All the α -Fe₂O₃ photoanodes show a positive slope in the dark (Fig. S4a) indicating that the hematite is n-type semiconductor with electrons as the majority carriers.

According to Fig. 6, the E_{fb} of the hematite range from 0.4 to 0.3 V (vs. RHE), and the donor density of 95-5 and 125-3 photoanodes are higher than others photoanodes, corresponding to the higher photocurrent density. Under illumination, slight or no increase is observed in the donor density for the all hematite photoanodes, proving that there is serious recombination between the photogenerated electrons and holes. Associated Fig. S4 and Fig. 5, comparing the photoanodes with nanorods morphology obtained at lower aging temperature and medium aging time to which with nanospheric columns obtained at higher aging temperature, the former have average onset potential (V_{onset}) of 0.57 V (vs. RHE.) and flat band potential of 0.36 V (vs. RHE.), the later have average onset potential of 0.69 V (vs. RHE.) and flat band potential of 0.32 V (vs. RHE.). The measured onset potentials of photocurrent can be directly related to the flat band potential since flat band potential is theoretically equal to onset potential of photocurrent. However it can be seen that the morphology has minor effect on flat band potential but greater effect on onset potential. The nanorod photoanodes have 0.12 V negative shift in the onset potential of photocurrent compared with nanocolumns photoanodes, which may be due to less electron traps and surface defects as nanorod photoanodes have lesser proportion of terminal oxygen ions.

A linear potential scan is used to determine the valence band maximum (VBM) energy levels of the hematite photoanodes [57]. Fig. S5 show the abrupt current increase revealed a VBM of 1.65 V (vs. RHE.) without illumination. By summarizing the data from the optical and electrochemical measurements, energy level diagram for the hematite photoanodes is constructed, as shown in Fig. 5(d), in which, the energy in the absolute vacuum scale (AVS) can be converted from the values of electrochemical scale using $E_{AVS} = -E_{RHE} - 4.5$. The energy level diagram also depicts the potentials for O_2 evolution from water decomposition. In the photoelectrochemical water splitting system, the holes generated in valence band transfer to the photoanode surface for water oxidation, and photogenerated electrons of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes must travel through the conduction band of the hematite semiconductor through the FTO conducting base layer to platinum cathode. In case of water oxidation in the light-driven oxygen evolution reaction (LOER), the driving force for the reaction is determined by the free energy difference ΔE_F between pE_F at the surface and the equilibrium redox Fermi level for the O_2/H_2O couple, which is defined as the overpotential $\eta_a = \Delta E_F / q$ [58]. The overpotential is large for $\alpha\text{-Fe}_2\text{O}_3$ photoanodes due to the accumulation of holes at the interface as a

consequence of sluggish electron transfer kinetics. The nanorod $\alpha\text{-Fe}_2\text{O}_3$ photoanodes is oriented in the [110] preferential direction without Ostwald bending, which is dominated by Fe(III) stoichiometric termination and has less electron traps and surface defects [59]. Then the nanorod $\alpha\text{-Fe}_2\text{O}_3$ photoanodes need lower overpotential for water oxidation compared with nanocolumn photoanodes, and the free energy difference $q\Delta\eta_a$ between them is equal to 0.12 eV as shown in Fig. 5(d).

To explore the charge transport dynamics in the electrodes, the electrochemical impedance spectroscopy (EIS) are measured at 0.23 V (vs. Ag/AgCl) and illumination, which is the same condition as the photocurrent measurements. Fig. 7a, b, c show the Nyquist impedance of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes analyzed in a frequency range of 0.1-10⁵ Hz, and the inset reveals the magnification of high frequency. The EIS data are fitted into an equivalent circuit model including two RC (a sub-circuit containing a resistance and a capacitance in parallel) circuits using the EIS spectrum analyzer software, where the dots in the plots represent the experimental data and the solid lines represent the result of fitting. The fitted impedance parameter values of the resistances (R) and constant phase elements (CPE) are listed in Fig. 5d. Holes generated inside the $\alpha\text{-Fe}_2\text{O}_3$ layer transfer to the electrolyte to oxidize water, and the R2/CPE2 is assigned to the electron transport inside the electrode. The RC circuit with the larger resistance (R1/CPE1) represents interface between n-type semiconductor electrode and electrolyte, which is the most difficult process of an entire photoelectrochemical reaction system due to slow charge transfer kinetics caused by energy mismatching between the acceptor *d* orbitals of hematite and donor *p* orbitals of the O₂-OH⁻ redox couple [60-62]. The fitting results indicate that the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes with vertical nanorods exhibit lower resistance values (R1 and R2), in accordance with the outstanding photocurrent response of 95-3, 95-4, 95-5, 95-6, and 125-3 photoanodes. The main reason is that the nanorods grown in the [110] direction to the FTO conducting base layer would eliminate grain boundaries, provide a direct path for electron collection, and allow photogenerated holes to reach the interface efficiently at the same time. In the samples mentioned above, the optimal photocurrent response of 95-5 and 125-3 photoanodes are due to the common action of higher absorbance and lower resistance.

The IPCE of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes are calculated by measuring the photocurrent under

monochromatic light at 0.23 V (vs. Ag/AgCl) according to the equation:

$$\text{IPCE}(\%) = \frac{1240 \times J}{\lambda \times P_{\text{mono}}} \times 100 \quad (2)$$

where J is photocurrent density (mA cm^{-2}), λ is wavelength of incident light (nm), and P_{mono} is incident light power density (mW cm^{-2}). The IPCE of the hematite photoanodes are shown in Fig. 8. It can be seen that the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes with vertical nanorods exhibit higher IPCE values, in accordance with the outstanding photocurrent response of 95-3, 95-4, 95-5, 95-6, and 125-3 samples. Meanwhile, it can be seen that the IPCE of the $\alpha\text{-Fe}_2\text{O}_3$ photoanodes in the short wavelength region is significantly higher than that in the long wavelength region. The electron-hole pairs irradiated by long wavelengths are located deep in the semiconductor bulk, and the low mobility combined with the small diffusion length of holes results in a high probability of recombination. In contrast, the photo-generated electron-hole pairs under short wavelengths do not have to diffuse a long distance to oxidize the water due to generating in the near-surface region with the existence of space charge layer.

4. Conclusions

$\alpha\text{-Fe}_2\text{O}_3$ photoanodes with different morphology, such as nanorods, nanocolumns, are successfully prepared by controlling the hydrothermal synthesis parameters of aging temperature and time. With increasing reaction temperature, Ostwald bending leads to larger tilt degree to isotropic growth. Furthermore, the photoelectrochemical measurement demonstrates that the as-obtained $\alpha\text{-Fe}_2\text{O}_3$ nanostructures show structure-dependent photoelectrochemical response. The optimal $\alpha\text{-Fe}_2\text{O}_3$ nanorods photoanodes can be obtained from 95 °C and 5 h, with 100 nm in diameter and 300 nm in thickness, which have the optimal photocurrent density up to 0.54 mA cm^{-2} and 0.12 V negative shift in the onset potential of photocurrent compared with nanocolumns photoanodes. The enhanced photoelectrochemical response is mainly attributed to the reduced resistance of the charge transfer inside the electrode and across interface of electrode and electrolyte as revealed by EIS analysis. The $\alpha\text{-Fe}_2\text{O}_3$ nanocolumn photoanodes can be obtained under higher temperature such as 155 °C, and in which the optimal photocurrent density of 0.23 mA cm^{-2} can be obtained under 155 °C (3 h) with 500 nm in diameter.

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Fig. 1. High magnification top-view SEM images of the α -Fe₂O₃ photoanodes synthesized at 95 °C, 125 °C and 155 °C for 3 h, 4 h, 5 h and 6 h (All the samples have the same scale bar)

Fig. 2. Cross-sectional SEM images of the α -Fe₂O₃ photoanodes synthesized at 95 °C, 125 °C and 155 °C for 3 h, 4 h, 5 h and 6 h.

Fig. 3. (a) X-Ray diffraction patterns of the α -Fe₂O₃ photoanodes synthesized at 95 °C, 125 °C and 155 °C for 3 h, 4 h, 5 h and 6 h. The standard patterns of α -Fe₂O₃ is depicted in the lower panels. (b) (c) (d) UV-vis absorbance spectra of the photoanodes; inset shows the digital images of the photoanodes.

Fig. 4. Schematic illustration for the growth process of β -FeOOH and α -Fe₂O₃ film

Fig. 5. (a)(b)(c) Photocurrent densities-potential curves in the dark (dashed lines) and under simulated solar light irradiation (solid lines) of the α -Fe₂O₃ photoanodes (AM 1.5 global, 1 sun (100 mW cm⁻²)). (d) Energy diagram and expected charge flow of the photoanode in 1M NaOH solution at pH=13.6.

Fig. 6. (a) Flatband potential and, (b) donor density of the α -Fe₂O₃ photoanodes in dark and under simulated solar light irradiation (AM 1.5 global, 1 sun (100 mW cm⁻²)).

Fig. 7. (a)(b)(c) Nyquist plots of the α -Fe₂O₃ photoanodes, (d) Corresponding equivalent circuit model and fitting impedance parameter values.

Fig. 8. Incident photo to current conversion (IPCE) of the α -Fe₂O₃ photoanodes.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8