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Graphic Abstract

A Novel In-situ Preparation Method of Nanostructured $\alpha$-$\text{Fe}_2\text{O}_3$ Films from Electrodeposited Fe Films for Efficient Photoelectrocatalytic Water Splitting and Organic Pollutant Degradation

Qingyi Zeng, Jing Bai, Jinhua Li, Ligang Xia, Ke Huang, Xuejin Li and Baoxue Zhou

Highly photoactive $\alpha$-$\text{Fe}_2\text{O}_3$ films prepared from novel electrodeposited Fe films were reported for PEC water splitting and organic pollutant degradation.
A Novel In-situ Preparation Method of Nanostructured $\alpha$-Fe$_2$O$_3$ Films from Electrodeposited Fe Films for Efficient Photoelectrocatalytic Water Splitting and Organic Pollutant Degradation

Qingyi Zeng, Jing Bai, Jinhua Li, Ligang Xia, Ke Huang, Xuejin Li and Baoxue Zhou

A novel preparation method was reported for preparing nanostructured hematite ($\alpha$-Fe$_2$O$_3$) films used in efficient photoelectrocatalytic (PEC) water splitting and organic pollutant degradation. The method includes two processes, namely the electrodeposition of Fe films in alkaline aqueous electrolyte with ferrisulfas and ammonia and the in-situ thermal oxidation of Fe films to obtain $\alpha$-Fe$_2$O$_3$ films. The thickness and crystallinity of the $\alpha$-Fe$_2$O$_3$ films can be precisely controlled by adjusting electrodeposition durations and annealing conditions, respectively, and the microstructured defects from traditional electrodeposition of FeOOH films and the undesired phases of FeO and/or Fe$_2$O$_3$ from thermal oxidation of Fe foils can be avoided, which facilitates the generation and transport/collection of photo-generated charges in the as-prepared $\alpha$-Fe$_2$O$_3$ films. The optimized $\alpha$-Fe$_2$O$_3$ film, which was obtained from a Fe film deposited for 30 s and then annealed at 500 °C for 2 h, showed a stable PEC water oxidation current of $\sim$1.35 mA cm$^{-2}$ at 1.23 V (vs. reversible hydrogen electrode, RHE) under AM 1.5 irradiation, which was the highest current obtained so far using undoped $\alpha$-Fe$_2$O$_3$ films from electrodeposition. When further decorated with Co-Pi co-catalyst, the optimized Co-Pi/$\alpha$-Fe$_2$O$_3$ photoanode showed incident photon-to-current conversion efficiencies (IPCE) higher than 18% at 400 nm with a stable photocurrent of $\sim$1.89 mA cm$^{-2}$. The as-prepared $\alpha$-Fe$_2$O$_3$ film also showed excellent stability and degradation efficiency (rate constant $\sim$0.9372 h$^{-1}$) for PEC degradation of MB in neutral aqueous solution under a positive bias potential.

1. Introduction

The extensive use of cheap and plentiful energy in the form of fossil fuels has brought tremendous revolutions in both human life and nature world. However, the fossil fuels cannot last forever, and the environment has already been and is still being impacted by the burning of fossil fuels. In order to reduce fossil fuel consumption and address the pressing environmental problems, the idea of improving the utilization of clean energy, such as solar energy, has been widely recognized. It is inspiring enough that a photoelectrocatalytic (PEC) technique has been developed to solve these problems by using solar light to drive water splitting and/or organic pollutant degradation since the pioneering work reported by Fujishima and Honda.1-3

Among various intensively studied semiconductor materials (e.g. TiO$_2$, ZnO, WO$_3$),10-14 hematite ($\alpha$-Fe$_2$O$_3$) is considered as one of the promising materials in this category, because of its small band gap ($\sim$2.1 eV) that enables it to harvest around 40% of the solar spectrum (up to $\sim$600 nm wavelength), excellent stability under alkaline conditions, environmentally benign characteristics, natural abundance, and low cost.15-19 However, the PEC activity of $\alpha$-Fe$_2$O$_3$ is limited by several factors, including the short lifetime of photogenerated charge carriers ($<$10 ps), short hole diffusion length ($\sim$2-4 nm), and a poor oxygen evolution reaction kinetics.20-24 To address these limitations, a number of strategies have been developed to improve the PEC properties of $\alpha$-Fe$_2$O$_3$: modifying electronic structure via elemental doping,25-27 synthesizing nanostructured $\alpha$-Fe$_2$O$_3$ (shorten the pathway that photoexcited electrons/holes have to travel),28,29 integrating $\alpha$-Fe$_2$O$_3$-based composite photoanode with better conducting material,30,31 and decorating the surface of $\alpha$-Fe$_2$O$_3$ with co-catalyst, such as cobalt phosphate (Co-Pi), to facilitate oxygen evolution reaction (OER).32,33

A novel preparation method was reported by Fujishima and Honda.143 photoelectrode, which is the key of the PEC technique for converting solar energy to chemical energy, such as PEC water splitting and waste water treatment.4-9 Among various intensively studied semiconductor materials (e.g. TiO$_2$, ZnO, WO$_3$), hematite ($\alpha$-Fe$_2$O$_3$) is considered as one of the promising materials in this category, because of its small band gap ($\sim$2.1 eV) that enables it to harvest around 40% of the solar spectrum (up to $\sim$600 nm wavelength), excellent stability under alkaline conditions, environmentally benign characteristics, natural abundance, and low cost.15-19 However, the PEC activity of $\alpha$-Fe$_2$O$_3$ is limited by several factors, including the short lifetime of photogenerated charge carriers ($<$10 ps), short hole diffusion length ($\sim$2-4 nm), and a poor oxygen evolution reaction kinetics.20-24 To address these limitations, a number of strategies have been developed to improve the PEC properties of $\alpha$-Fe$_2$O$_3$: modifying electronic structure via elemental doping,25-27 synthesizing nanostructured $\alpha$-Fe$_2$O$_3$ (shorten the pathway that photoexcited electrons/holes have to travel),28,29 integrating $\alpha$-Fe$_2$O$_3$-based composite photoanode with better conducting material,30,31 and decorating the surface of $\alpha$-Fe$_2$O$_3$ with co-catalyst, such as cobalt phosphate (Co-Pi), to facilitate oxygen evolution reaction (OER).32,33
Numerous methods have been reported for preparing α-Fe$_2$O$_3$ photoanode, including hydrothermal, spray pyrolysis, DC magnetron sputtering, electro deposition, atmospheric pressure chemical vapor deposition (APCVD), atomic layer deposition (ALD), and anodization. Among these methods, electrodeposition is a facile and cost-effective method for the α-Fe$_2$O$_3$ film preparation.

The reported electrodeposition method for preparing α-Fe$_2$O$_3$ films includes the following two steps: first, the electrodeposition of FeOOH films; and second, the calcination of it. This method is divided into cathodic electrodeposition and anodic electrodeposition based on the difference of the electrolyte. The cathodic electrodeposition includes the electrochemical reduction of H$_2$O$_2$ in order to form OH$^-$ in a solution containing Fe$^{3+}$ and subsequently the precipitation of Fe$^{3+}$ to form FeOOH films near the cathode. The Fe$^{3+}$ ions can be precipitated as a result of the increased local pH near the cathode to facilitate the formation of FeOOH films. The anodic electrodeposition, on the other hand, involves the oxidation of Fe$^{2+}$ to Fe$^{3+}$ and the following precipitation of Fe$^{3+}$ for the development of FeOOH films near the anode. The prepared FeOOH films can be converted to α-Fe$_2$O$_3$ films by calcination. In sum, the processes for FeOOH films formation in both the cathodic electrodeposition and the anodic electrodeposition are realized from the direct transformation of Fe$^{2+}$ or Fe$^{3+}$ to FeOOH films, which includes the reduction of H$_2$O$_2$ to form OH$^-$, the oxidation of Fe$^{2+}$ to form Fe$^{3+}$, the precipitation of Fe$^{3+}$ to form FeOOH, the annealing of the FeOOH film to form the α-Fe$_2$O$_3$ film, and so on. In this complicated process, various complex compounds of Fe$^{2+}$ and Fe$^{3+}$ in aqueous solution, such as polyhydroxy compounds, polynuclear complex, and Bridging ligand compounds would form near the working electrode, causing unavoidable microstructured defects in the as-deposited FeOOH film, which would further be introduced into the final α-Fe$_2$O$_3$ structure. Therefore, both cathodic electrodeposition and anodic electrodeposition can hardly produce orderly arranged FeOOH films.

Several works reported the preparation of α-Fe$_2$O$_3$ films via direct thermal oxidation of Fe foils, which is an in-situ, simple and promising way to prepare α-Fe$_2$O$_3$ photoelectrode. Different iron oxide structures can be directly formed on the Fe foils under different annealing conditions and this simple air oxidation of iron can provide a short path to form hematite nanowires. However, the thickness and crystallinity of the oxide film could be difficult to control due to the rapid oxidation of metal Fe during thermal oxidation of the Fe foil. Furthermore, the presence of FeO and/or Fe$_2$O$_4$ at the interface of metallic Fe and Fe$_2$O$_3$ could be unavoidable. As a result, the photoresponse of the prepared α-Fe$_2$O$_3$ photoelectrode is quite poor.

Based on the above discussion, we propose a novel method to prepare α-Fe$_2$O$_3$ films, which combines the virtues of both electrodeposition and thermal oxidation while avoids their defects. Specifically, the α-Fe$_2$O$_3$ film was obtained via direct electrodeposition of Fe films on the conductive substrate, such as F-doping tin oxide (FTO) coated glass, in alkaliescent conditions by adding superfluous ammonia in ferrous sulfate solution, and followed by in-situ thermal oxidation of Fe films to create α-Fe$_2$O$_3$ films. This method has several advantages: i) it ensures the uniformity of the deposited Fe film and the resulted α-Fe$_2$O$_3$ film as the alkaliescent condition should prevent the corrosion of the as-deposited Fe; ii) it should facilitate the deposition of the Fe film in an orderly arrangement since the existence of ferrous hydroxide compounds keeps the reduction rate of Fe$^{2+}$ to Fe moderately, which prevents the generation of microstructured defects in the deposited film, distinguishing it from the traditional strategies such as the direct electrodeposition of FeOOH films from Fe$^{2+}$ or Fe$^{3+}$; iii) it prevents the presence of undesired phases of FeO and/or Fe$_2$O$_4$ appearing in the traditional thermal oxidation of Fe foils because the uniform and tunable Fe film on the FTO substrate can be transformed into α-Fe$_2$O$_3$ completely; iv) it facilitates the generation and transport/collection of photo-generated charges in the as-prepared α-Fe$_2$O$_3$ film for its tunable thickness, pure phase and lesser microstructured defects.

In this work, the feasibility of using the above described facile method to prepare highly photoactive α-Fe$_2$O$_3$ films for efficient PEC water splitting and organic pollutant degradation has been investigated. The result indicates that the as-deposited Fe film can be completely converted into α-Fe$_2$O$_3$, and the thickness and the crystallinity of the α-Fe$_2$O$_3$ film are tunable via adjusting the deposition durations of the Fe film and annealing conditions, respectively. The effects of annealing temperature and annealing time on PEC water splitting performance of α-Fe$_2$O$_3$ films were observed, respectively. Co-Pi decorated α-Fe$_2$O$_3$ films were also prepared via photo-assisted electrodeposition to increase the oxygen evolution reaction efficiency at a decreased over-potential. Finally, the effect of PEC organic pollutant degradation with the α-Fe$_2$O$_3$ films was examined.

2. Experimental

2.1. Synthesis of α-Fe$_2$O$_3$ Film

The Fe film was first electrodeposited on the F-doping tin oxide (FTO) coated glass substrate (13 Ωcm$^{-1}$) in a two-electrode configuration with the FTO glass working as cathode and a platinum foil as anode (see Fig. 1 and Fig. S1†). The distance between the cathode and the anode was ~3 cm. The electrolyte was prepared by dissolving 5 g FeSO$_4$·7H$_2$O and 30 mL ammonia (27%) in 150 mL deionized water (the tested pH=10.8 at 25 ºC). The electrodeposition was carried out at 2 V for 15, 30, 45 and 60 s with a vigorous stirring. The as-deposited Fe film was rinsed with deionized water for 5 min and then dried at 50 ºC with a gentle stream of nitrogen gas for 1 h, which was followed by thermal oxidation in air.
Deposition of Co-Pi on the surface of the as-prepared α-Fe₂O₃ film was carried out in a three-electrode system with the α-Fe₂O₃ film used as the working electrode, a platinum foil as the counter electrode and a saturated calomel electrode (SCE) as the reference via photo-assisted electrodeposition (PED) method. 0.1 M sodium phosphate buffer solution at pH 7 containing 5 mM Co(NO₃)₂ was used as an electrolyte. The PED was carried out at 0.1 V under the illumination of 1 sun-simulated solar light. After PED, the α-Fe₂O₃ film modified with Co-Pi was rinsed with deionized water for 5 min and then dried at 50 °C for 1 h.

2.2. Characterization

The morphologies and microstructures of the samples were investigated by FE-SEM (Sirion200, Philips, Netherlands) equipped with an energy dispersive X-ray detector (EDX). XPS spectra were measured with an AXIS Ultra DLD (Kratos, Shimadzu) using non-chromatic Al Kα radiation at 12 kV and 25 mA. The crystal phase of the samples was characterized with X-ray diffractometry (XRD) (AXS-8 Advance, Bruker, Germany). Raman spectra were recorded on SPECTRUM R200 system (Bruker, Germany) with laser excitation of 532 nm. UV–visible absorption spectra of the samples were recorded on a UV–Vis photospectrometer (TU-1901, Peneral, China).

2.3. Photoelectrocatalytic Measurements

The photoelectrocatalytic (PEC) water splitting experiments were carried out in 1 M KOH electrolyte using a three-electrode system with an SCE as the reference, a platinum foil as the auxiliary electrode, and as-prepared films as the working electrode. The PEC tests were controlled by an electrochemical workstation (CHI 660c, CH Instruments Inc., USA). A 350 W Xe lamp (Shanghai Hualun Bulb Factory) with AM 1.5 filter was used for light illumination (light density: 100 mW cm⁻²). Incident-photon-to-charge conversion efficiency (IPCE) was measured by a system comprising a monochromator (Zolix, China), a 500 W xenon arc lamp, a calibrated silicon photodetector, and a power meter.

The PEC degradation of Methylene Blue (MB) experiment was conducted under the following conditions: AM 1.5 irradiation, vigorous stirring, 0.6 V (vs. SCE) of electric bias, pH 7, and 0.01 mol L⁻¹ sodium sulfate as supporting electrolyte. The photocatalytic (PC) degradation was performed without applying an external potential on the working electrodes. The initial concentration of MB solution was 5 mg L⁻¹ and the reaction solution was 25 mL during the experiment. At different time intervals, the reaction solution was analyzed using a UV–Vis spectrophotometer (UV2102 PCS, UNICO, Shanghai).

The IMPS was tested by using an electrochemical workstation (ZENNIUM, ZAHNER-elektrik GmbH&Co.KG, Germany) equipped with a controlled-intensity-modulated-photospectroscopy setup (CIMPS, PP211, ZAHNER-elektrik GmbH&Co.KG, Germany) following a three-electrode configuration with the prepared α-Fe₂O₃ film working as the working electrode, a platinum foil as the counter electrode, and an SCE as the reference electrode with a 1 M KOH electrolyte. A white light lamp (WLC02, ZAHNER-elektrik GmbH&Co.KG, Germany) was used as the light source. The modulated light in the frequency range of 0.1 Hz – 10 KHz superimposed on a steady DC light intensity of 80 mWcm⁻² was applied. The bias potential applied on the working electrode was 0.23 V vs. SCE.

3. Results and Discussion

3.1. Fabrication of α-Fe₂O₃ Film

In this work, we have provided an alternative way to prepare Fe films via electrodeposition in ammonia conditions. In order to reveal the effect of ammonia on the electrolyte, various electrolytes have been used for electrodepositing Fe films. The voltammetric curves carried out on FTO substrates in different electrolytes are shown in Fig. 2. As can be seen from Fig. 2, the onset potential increased after the pH was adjusted by NaOH, even though the pH was the same, suggesting that the reaction occurring on the FTO substrate in the electrolyte with ammonia was different from that in the electrolyte with NaOH.
speculation is verified by the XRD patterns of the deposited films from the electrolyte with NaOH shown in Fig. S2,† which indicates that the deposited films were tetragonal Sn films. However, the XRD patterns of the as-deposited film from the electrolyte with ammonia shown in Fig. 3(A) indicate that it was cubic Fe film. From the inset paragraph in Fig. 1, this Fe film showed good uniformity with a matte black color, and was well adherent to the substrate. Thus, the ammonia condition leads to a significant enhancement of the uniformity of the as-deposited Fe film and prevents the reduction of SnO₂ in strong alkaline (NaOH) condition. (Detailed discussion seen ESI†)

![Fig. 3 XRD patterns of α-Fe₂O₃ film (deposited for 30 s) annealed at (A) different temperatures for 2 h, (B) 500 °C for various durations.](image)

The as-deposited Fe films were annealed in the air at different temperatures for different durations, and their XRD patterns are shown in Fig. 3. Fig. 3(A) shows the XRD patterns of Fe film annealed at different temperatures ranging from 300 to 700 °C for 2 h. It can be seen that the as-deposited Fe film with cubic phase changed to amorphous phase at 300 °C and the characteristic peaks of α-Fe₂O₃ (JCPDS no.890598) appeared at 400 °C. When annealed at 500 °C, the intensity of (110) peak became the strongest among the samples. With the annealing temperature further increased, the intensity of (104) peak increased at 600 °C, and (012) peak appeared at 700 °C.

Fig. 3(B) gives the XRD patterns of Fe film annealed at 500 °C for different durations. (110) peak of hematite structure appeared after being annealed for 0.5 h and it was intensified with a longer annealing time of 2 h. With longer annealing time, a new (012) peak appeared and the intensity of the (104) peak was high purity with α-Fe₂O₃. The Raman spectra shown in Fig. 4(A) exhibit the characteristic peaks of α-Fe₂O₃ at 212, 271, 384, 484, 579, and 1282 cm⁻¹, which is distinct from the values from Fe₂O₃ (~709 eV) and FeO (709.1–709.5 eV). A characteristic satellite peak of α-Fe₂O₃ also appeared at 718.8 eV. In general, these results confirmed that α-Fe₂O₃ thin films can be synthesized with a pure phase via a route including electrodeposition of Fe film in electrolyte with ammonia and the following in-situ thermal oxidation in air.

![Fig. 4 (A) Raman spectra, (B) XPS survey data, and (C) Fe 2p core-level spectra of α-Fe₂O₃ film (deposited for 30 s, annealed at 500 °C for 2 h).](image)

The typical SEM image of the as-deposited Fe film is shown in Fig. S3.† As we can see, the Fe film consists of nanoparticles, and the surface is relatively smooth. Fig. 5 shows the SEM micrographs of α-Fe₂O₃ films (500 °C for 2 h) from Fe films obtained with different deposition times. Fig. 6 shows the corresponding cross-section SEM images. After annealed in the air, the nanoparticle-like Fe films were transformed into compact α-Fe₂O₃ films, especially for the sample with 5 min deposition. The surface morphology of the samples is shown in the figure (Fig. 5(A)). The α-Fe₂O₃ film of the samples deposited for 30 s, 45 s and 60 s appear a similar surface morphology showing a compact film with some nanoparticles on the surface. All the as-prepared α-Fe₂O₃ films were well adherent to the FTO substrate, and the...
thickness of the film was linear dependence with the deposition time (Fig. 6 and Fig. S4†).

The PEC water splitting activity of the α-Fe$_2$O$_3$ films was studied in a three-electrode PEC cell to observe their PEC water oxidation response in 1 M KOH under simulated solar light irradiation (100 mWcm$^{-2}$, AM 1.5). The potentials were measured relative to the saturated calomel electrode (SCE) reference electrode and converted to the reversible hydrogen electrode (RHE) scale according to the following equation:

$$E_{\text{RHE}} = E_{\text{SCE}} + 0.0591 \times \text{pH} + E_{\text{SCE}}^0,$$

where the $E_{\text{RHE}}$ is the calculated potential versus RHE, $E_{\text{SCE}}$ is the measured potential, pH is about 13.9 and $E_{\text{SCE}}^0$ is about 0.2415 V at 25 ºC. The photocurrent densities measured at 1.23 V vs. RHE of the α-Fe$_2$O$_3$ films annealed at different temperatures for 2 h are shown in Fig. 8 (A). The α-Fe$_2$O$_3$ film annealed at 500 ºC showed the highest photocurrent density of ~1.35 mA cm$^{-2}$, while the Fe$_2$O$_3$ film annealed at 300 ºC showed the lowest photocurrent, possibly because the insufficient crystallization of the film leads to a higher defect density and lower conductivity. The α-Fe$_2$O$_3$ film annealed at 600 ºC showed a smaller photocurrent than that of the sample annealed at 500 ºC, which should be attributed to the rapid increase of resistance of the FTO film (see Fig. S5†). The increased resistance can also explain the decrease of photocurrent of the sample annealed at 700 ºC. Moreover, the decreased absorption intensity in the region of 320-500 nm of the sample annealed at 700 ºC should also account for the
decrease of photocurrent. Fig. 8(B) shows the photocurrent densities of α-Fe₂O₃ films annealed at 500 °C for different times. The sample annealed for 0.5 h showed the lowest photocurrent of ~0.8 mA cm⁻², while the highest photocurrent of ~1.35 mA cm⁻² was obtained for the sample annealed for 2 h. When the annealing time was further increased, the photocurrent decreased slightly. According to the XRD patterns (Fig. 3) and the UV-Vis absorption spectra (Fig. 7), the α-Fe₂O₃ film showing the strongest (110) peak in the XRD patterns could have marvelously improved photocurrent density (the α-Fe₂O₃ films annealed at 500 °C for 2 h vs. 400 °C for 2 h or 500 °C for 0.5 h). However, the sample with the (012) peak showed relatively small photocurrent density (the α-Fe₂O₃ films annealed at 500 °C for 4 h or 6 h, or 700 °C for 2 h). This interesting result should be due to the superior conductivity of α-Fe₂O₃ along the [110] direction compared with that in the orthogonal direction mentioned above.

![Fig. 9 Photocurrent-potential (I-V) curves with chopped light for PEC water oxidation reaction of the α-Fe₂O₃ films deposited for different durations (annealed at 500 °C for 2 h) measured in the 1 M KOH electrolyte under AM 1.5 illumination.](image)

Fig. 9 shows the chopped photocurrent-potential (I-V) curves of the α-Fe₂O₃ films with different deposition times (annealed at 500 °C for 2 h). Obviously, the sample with a deposition time of 30 s showed the highest photocurrent response among the four tested samples. However, further increase of the deposition time reduced the PEC water oxidation performance. For example, the sample 60 s showed the lowest photocurrent response. As aforementioned, α-Fe₂O₃ is an indirect band gap semiconductor with a very short lifetime of photogenerated charge carriers (<10 ps) and short hole diffusion length (~2-4 nm).²⁴ Although the increase of film thickness would improve the light absorption for generating more photocharges, it would also increase the recombination rate of photogenerated electron-hole pairs and decrease the efficiency of charge transfer. It means that the benefit from enhanced light absorption could be offset by rapidly increasing recombination rate, especially in the excessively thick film. Hence, a suitable thickness of α-Fe₂O₃ film would be crucial for both light absorption and charge transfer in PEC application. In this work, the optimum sample (30s) contains an α-Fe₂O₃ film with a thickness of ~230 nm (Fig. S4).†

Cobalt–phosphate (Co–Pi) is an efficient surface water-oxidation co-catalyst that can improve the water oxidation kinetics on the photoanode surface in PEC water splitting.³³,⁵⁶,⁵⁷ So, in order to improve the performance of the prepared α-Fe₂O₃ film in PEC water splitting, Co–Pi decorated α-Fe₂O₃ films (Co–Pi/α-Fe₂O₃) with different photo-assisted electrodeposition (PED) times were prepared. The EDX result of the prepared 600 s Co–Pi/α-Fe₂O₃ film (600 s represents the deposition time of Co–Pi) shown in Fig. S6† indicates that Co–Pi was decorated on the α-Fe₂O₃ film uniformly. The I-V curves of the Co–Pi/α-Fe₂O₃ films with different PED times are shown in Fig. 10(A). As can be seen from Fig. 10(A), the decoration of Co–Pi on the α-Fe₂O₃ film could reduce the onset potential of the photoanode for water splitting under both light illumination and dark, which means Co–Pi can facilitate the water oxidation reaction taking place at Fe₂O₃|electrolyte. With deposition of Co–Pi for 300 s, the photocurrent response of the sample increased remarkably from ~1.35 mA cm⁻² to ~1.72 mA cm⁻² at 1.23 V vs. RHE. With the PED time further increased to 600 s, the photocurrent response increased slightly with a photocurrent of ~1.89 mA cm⁻². However, the photocurrent response fell to ~1.53 mA cm⁻² after 1200 s PED. As can be seen from the Nyquist plots of these samples shown in Fig. 10(B), Co–Pi could decrease the resistance of the α-Fe₂O₃ films in PEC water splitting, and 600 s Co–Pi/α-Fe₂O₃ photoanode showed the lowest resistance. However, a thicker Co–Pi layer, such as 1200 s Co–Pi/α-Fe₂O₃, would increase the resistance in the Co–Pi layer itself and finally reduce the charge transfer properties. Therefore, 600 s is the optimum time for deposition of Co–Pi on the α-Fe₂O₃ film in this case.

![Fig. 10 (A) Photocurrent-potential (I-V) curves with chopped light for PEC water oxidation reaction of the Co–Pi/α-Fe₂O₃ films with different photo-assisted electrodeposition times; (B) Nyquist plots of the Co–Pi/α-Fe₂O₃ photoanodes under 1.23 V vs. RHE. The measurements were done in the 1 M KOH electrolyte under AM 1.5 illumination.](image)

![Fig. 11 (A) The photocurrent-time curves and (B) IPCE plots of α-Fe₂O₃ photoanode and 600s Co–Pi/α-Fe₂O₃ photoanode measured at 1.23 V vs. RHE in the 1 M KOH electrolyte.](image)
The stability of the prepared photoanode in PEC water splitting is crucial for both fundamental and practical studies. Fig. 11(A) shows the photocurrent curves of optimized α-Fe₂O₃ photoanode and Co–Pi/α-Fe₂O₃ photoanode measured at 1.23 V vs. RHE in the 1 M KOH electrolyte under AM 1.5 illumination for 2 h. The photocurrent of α-Fe₂O₃ photoanode and 600 s Co–Pi/α-Fe₂O₃ photoanode were ~1.34 mA cm⁻² and ~1.85 mA cm⁻², respectively, without any significant decline, indicating that both photoanodes exhibited excellent stability in PEC water splitting. To quantitatively investigate the photoactivity of the α-Fe₂O₃ films as a function of wavelength, Incident-photon-to-charge conversion efficiency (IPCE) measurements were performed on the optimized α-Fe₂O₃ photoanode and Co–Pi/α-Fe₂O₃ photoanode at 1.23 V vs RHE, and the result is shown in Fig. 11(B). The IPCE behaviors of both photoanodes were observed between 350 and 570 nm, which is roughly consistent with the light absorption spectrum of α-Fe₂O₃ film (see Fig. 7). This indicates that the absorbed photons with different energies have been converted to photocurrents successfully. The IPCE values of Co–Pi/α-Fe₂O₃ photoanode were higher than those of the bare α-Fe₂O₃ photoanode in the full response region, which means that the decoration of Co-Pi co-catalyst could make the absorbed photons with different energies convert to current more efficiently. The IPCE values in the short wavelength region (~380 nm) were up to ~22% for Co–Pi/α-Fe₂O₃ photoanode, much higher than those of the reported α-Fe₂O₃ film prepared via anodic or cathodic electrodeposition. Furthermore, it should be noted that it is a common characteristic of α-Fe₂O₃ photoanode that the IPCE curve has a more rapid decrease over 380–450 nm compared with the absorption spectrum (see Fig. 7). This is because the photons in this region only excite indirect d→d transition of Fe³⁺, which only generates electron-hole pairs localized in Fe²⁺ and cannot provide effective energy for water oxidation.²³,⁵⁸,⁵⁹

The PEC activity of the optimized α-Fe₂O₃ film was also investigated by organic compound degradation experiments. The PEC (at a bias potential of 0.6 V vs. SCE), photocatalytic (PC, PEC without bias potential), and direct photolytic (DP) degradation of MB in neutral aqueous solutions were performed under given conditions, respectively. Fig. 12(A) shows the UV–vis absorption spectra of MB solution after PEC reaction by the α-Fe₂O₃ film for different times. The characteristic peak of MB (at 665 nm) was found decreasing steadily with the reaction time. As shown in Fig. 12(B), the performance of the α-Fe₂O₃ film in different systems follows the tendency of PEC > PC > DP. The highest rate constant was ~0.937 2 h⁻¹ obtained by PEC, which is 5.06 and 9.12 times higher than that of PC (~0.1851 h⁻¹) and DP (~0.1028 h⁻¹), respectively. This result suggests that the presence of α-Fe₂O₃ film can improve the degradation efficiency of MB, especially under a positive bias for enhanced separation of photogenerated electron-hole pairs in the α-Fe₂O₃ film. Since the kinetic constant of PC reaction is only 1.8 times higher than that of DP reaction, it also indicates the poor transport property of photogenerated charges in the α-Fe₂O₃ film without a positive bias. The reusing test of the α-Fe₂O₃ film for PEC degradation of MB in three PEC cycles shown in Fig. 12(D) further indicates that the as-prepared α-Fe₂O₃ film is stable for PEC applications, such as organic compound degradation.

3.3. IMPS measurements

In order to illustrate the lesser microstructured defects in the α-Fe₂O₃ films prepared in this work, intensity modulated photocurrent spectroscopy (IMPS) has been applied to measure the charge carrier transit times (τₐ) in the α-Fe₂O₃ films prepared in this work and the anodic α-Fe₂O₃ films prepared via traditional anodic electrodeposition.²⁸ IMPS is a powerful, non-destructive characterization technique for analyzing the photogenerated carriers transportion and recombination/relaxation information in the photocathode.⁶⁰–⁶² The average time of photogenerated charges need to reach the back contact, the transit time τₐ, can be estimated from τₐ = (2πfₘᵢₙ(IMPS))⁻¹, where fₘᵢₙ is the frequency at the minimal value in the IMPS plot.⁶⁰ The transit time reflects the recombination probability of photogenerated electrons and holes in the photoelectrode, which is always related to the microstructure properties of the photoelectrode film.⁶²

The XRD patterns shown in Fig. S8† indicate that the annealed film consisted of α-Fe₂O₃, the same with what has been reported in the literature.²⁸ The SEM images shown in Fig. S9† indicate that the as-deposited FeOOH film and the anodic α-Fe₂O₃ film were uniform, and the thickness of the anodic α-Fe₂O₃ film was ~410 nm. For comparison, the α-Fe₂O₃ film with a deposition time of 60 s whose thickness was also ~410 nm (Fig. S4†) was selected for the IMPS test and this film was denoted as 60s/α-Fe₂O₃ film.

Fig. 13 shows the IMPS plots of the anodic α-Fe₂O₃ film and the 60s/α-Fe₂O₃ film. According to the fₘᵢₙ, the calculated τₐ values of the anodic α-Fe₂O₃ film and the 60s/α-Fe₂O₃ film are 3.004 ms and 1.197 ms, respectively. The transit time τₐ of the
anodic α-Fe₂O₃ film is nearly three-fold that of the 60s/α-Fe₂O₃ film. This result demonstrates that the photogenerated electron/hole transport easily reach the back contact in the 60s/α-Fe₂O₃ film when compared with the anodic α-Fe₂O₃ film. Since the nanostructured defects in the photoelectrode film can generate a lot of crystal boundaries which will impede the transport of charges and promote the recombination of photogenerated electron/hole, the IMPS result indicates that the α-Fe₂O₃ film prepared in this work should possess lesser nanostructured defects when compared with the anodic α-Fe₂O₃ film prepared via traditional electrodeposition method.

![Image](http://example.com/image.png)

**Fig. 13** The IMPS plots of the (a) anodic α-Fe₂O₃ film and (b) 60s/α-Fe₂O₃ film.

4. Conclusion

In summary, a facile method for preparing photocorrosion stable and highly photocative α-Fe₂O₃ films has been proposed in this work. The ammonia contained in the electrolyte is crucial to preparing the uniform Fe film via an electrodeposition method. The Fe film can be transformed into α-Fe₂O₃ film completely via in-situ thermal oxidation. The optimized α-Fe₂O₃ photoanode showed a stable PEC water oxidation current of ~1.35 mA cm⁻² at 1.23 V vs. RHE under AM 1.5 irradiation. After decorated with Co-Pi co-catalyst, the optimized Co-Pi/α-Fe₂O₃ photoanode showed IPCE higher than 18% at 400 nm with a stable photocurrent of ~1.89 mA cm⁻² for the PEC water splitting. The α-Fe₂O₃ photoanode also showed excellent stability and degradation efficiency (rate constant ~0.9372 h⁻¹) for PEC degradation of MB in neutral aqueous solution. This paper provides a useful insight into the design and fabrication of α-Fe₂O₃ photoanode for potentially cost-effective and highly-efficient PEC applications.

Acknowledgements

The authors would like to acknowledge the National Nature Science Foundation of China (Nos. 21276153, 21177085, 21207088), the Doctoral Program of the Ministry of Education of China (No. 20110073110029), and the Shanghai Basic Research Key Project (11JC1406200) and Shanghai Yangfan Program (14YF1401500) for financial support.

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