Synthesis of metal oxide photoanode with improved photoelectrochemical performance by hydrothermal method

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Abstract. Hematite photoanode was obtained through hydrothermal method. The physical and photophysical properties of the hematite photoanode were investigated by X-ray diffraction (XRD), UV-vis absorption spectroscopy, and the photoelectrochemical performance was also evaluated. In terms of maximizing the photoelectrochemical performances of the hematite photoanodes, the preparation conditions were optimized. And a possible mechanism was proposed to explain the reason for the improvement of photoelectrochemical performances.

Keywords: hydrothermal method, photoanode, photoelectrochemical.

1. Introduction

The production of hydrogen could be realized through the photo-electrolysis of water by Fujishima and Honda [1]. Photocatalysis technique has received more attention and been used to solve energy and environmental issues as a promising, clean and renewable strategy [2, 3]. As a classical semiconductor photocatalyst, TiO$_2$ has been widely studied, however, only a small fraction of the solar spectrum can be utilized by TiO$_2$ for its wide band gap. Thus, the improvement of the quantum efficiency is important for the wide application of a photoelectrode [4]. Hematite has gained significant attraction and been a promising material [5].

To improve the electronic transport properties in hematite and realize the high PEC performance with the application in a large scale by reducing the electron–hole recombination, a suitable synthesis method is also crucial for the hematite photoelectrodes. Recently, various synthesis methods have been reported to prepare hematite photoelectrodes, such as pulsed spin coating [6], spray-pyrolysis deposition (SPD) [7], hydrothermal method [8, 9], sol–gel route [10], and etc. Hydrothermal method among the synthesis techniques is a facile method to synthesize hematite photoelectrodes.

In the present study, hematite photoanode was prepared via hydrothermal method. The photoelectrochemical performances of the hematite photoanodes were analyzed and in terms of maximizing the photoelectrochemical performances of the hematite photoanodes, the preparation conditions were optimized.
2. Experimental

2.1. Materials
The starting materials utilized are FeCl$_3$·6H$_2$O, Fe(NO$_3$)$_3$·9H$_2$O and ethanol (Sinopharm Chemical Reagent Co. Ltd.). All reagents were of analytical purity grade.

2.2. Synthesis of $\alpha$-Fe$_2$O$_3$ photoanode
The F-doped tin oxide (FTO) covered glass substrates which were dipped in the ferric nitride ethanol solution and dried for three times and then calcined at 500 °C for 4h, were put on the bottom of a 50 mL Teflon-lined stainless steel autoclave. In the typical process, the reaction solution with FeCl$_3$·6H$_2$O (1.6217 g) and 0.4 g surfactant in deionized water (30 mL) was transferred into the Teflon-lined stainless steel autoclave. The autoclave was sealed, heated at different temperatures. The as-prepared $\alpha$-Fe$_2$O$_3$ thin films were washed with deionized water and absolute ethanol several times after being cooled down to room temperature.

2.3. Characterization
X-ray diffraction (XRD) measurements were performed on a Shimadzu 6000 X-ray diffractometer with Cu Kα radiation ($\lambda$ = 0.154 nm) and a scan rate of 10 °·min$^{-1}$. The light absorption was obtained using Ultraviolet visible (UV-vis) spectrophotometer by measuring the transmittance with an integrating sphere (Lambda 750S, Perkin-Elmer) and the absorption spectrawere obtained using the Kubelka–Munk method.

2.4. Photoelectrochemical (PEC) measurements
Photoelectrochemical properties were characterized by using a three-electrode configuration (PCI4/300™ potentiostat with PHE200™ software, Gamry Electronic Instruments, Inc.) in a standard three-electrode configuration coupled with the as-prepared sample films as the working electrode, anAg/AgCl electrode as the reference electrode and a highpurity Pt foil as the counter electrode. Thephotocurrents of water oxidation were measured in 1 M KOH aqueousolution with a scan rate of 20 mV·s$^{-1}$.

3. Results and Discussion
The XRD pattern of the Fe$_2$O$_3$ thin film prepared through hydrothermal method is shown in Fig. 1. As seen from Fig. 1, it shows that all peaks in the Fe$_2$O$_3$ sample are consistent with the characteristic pattern of $\alpha$-Fe$_2$O$_3$ structure (PDF card No. 33-0664), and no peaks of the impurity phases can be observed except for the marked FTO glass substrate’s peaks. The intense peaks of the XRD patterns indicate the well-crystallized $\alpha$-Fe$_2$O$_3$ thin films can be successfully prepared by the hydrothermal method.

![Fig. 1 XRD patterns of Fe$_2$O$_3$ film prepared through hydrothermal method and heated at 180 °C for 2 h.](image-url)
The light absorptions of the $\alpha$-$\text{Fe}_2\text{O}_3$ film samples prepared by hydrothermal method were measured using UV–vis absorption spectroscopy, which is shown in Fig. 2. It is observed from Fig. 2 that the $\alpha$-$\text{Fe}_2\text{O}_3$ film exhibits a broad absorption and possesses good absorption to visible light, and the visible light absorption of hematite is due to the $\text{Fe}^{3+}$ 3d-3d spin forbidden transition excitation[11]. The absorption edge of the as-prepared $\alpha$-$\text{Fe}_2\text{O}_3$ sample occur at ca. 605 nm.

**Fig. 2** The UV-vis absorption spectrum of $\alpha$-$\text{Fe}_2\text{O}_3$ film prepared by hydrothermal method.

The influence of hydrothermal reaction temperatures on the photo-electrochemical property of hematite samples after surface pretreatment is investigated. The photocurrent curves of the hematite samples prepared at different hydrothermal reaction temperatures are shown in Fig. 3. The result shows that the photocurrent obviously increases when the hydrothermal reaction temperatures are increased from 160°C to 180°C, which may be due to the improvement of the crystallization. While for the hematite sample prepared at 200°C, the photocurrent is lower than that of the sample prepared at 180°C through the hydrothermal route. Due to the easier recombination of photo-generated carriers induced by the relatively larger crystal size of the sample after reaction at higher temperature, the photocurrent may be decreased.

**Fig. 3** Photocurrent curves of the samples prepared at a. 160°C; b. 180°C; c. 200°C.
From Fig. 4, Fig. 5 and Fig. 6, low and high-resolution SEM images of the as-prepared hematite film prepared by the hydrothermal method for different temperatures are measured. From the SEM images, it can be observed that the planar surface structure is compact and no obvious cracks appear for the as-prepared hematite film prepared by the hydrothermal method at 160 °C. Thus, through hydrothermal method, the compact hematite films can be prepared. The obvious particles can be observed by SEM images on the surface of the as-prepared hematite films with the increasing hydrothermal reaction temperature. The photo-electrochemical efficiency of the as-prepared hematite film prepared by the hydrothermal method may be influenced by the reaction temperatures.

**Fig. 4** High-resolution SEM image of the surface of hematite film prepared by hydrothermal method at 160 °C.

**Fig. 5** SEM image of the surface of hematite film prepared by hydrothermal method at 200 °C.
Fig. 6 High-resolution SEM image of the surface of hematite film prepared by hydrothermal method at 200 °C.

4. Conclusions
In summary, hematite thin films were deposited through hydrothermal method. The preparation conditions were optimized to improve the photoelectrochemical performances of the hematite photoanode. The hematite photoanode prepared at 180 °C showed the highest photoelectrochemical performance.

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