Synthesis and the photoelectrochemical performance of Fe$_2$O$_3$ photoanode through pretreatment

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Abstract. The photo-electrochemical performance of hematite (α-Fe$_2$O$_3$) photoanode was evaluated and the preparation conditions were optimized in terms of maximizing the photoelectrochemical performances of the hematite photoanodes. The photoelectrochemical performances of hematite photoanode can be improved by the electrochemical surface pretreatment, and a possible mechanism was proposed to explain the reason for the improvement of photoelectrochemical performance.

Keywords: Iron oxide; pretreatment; photoelectrochemical.

1. Introduction

Since the production of hydrogen through the photo-electrolysis of water could be realized by Fujishima and Honda, to solve environmental and energy issues, photocatalysis technique has received more attention and been used as an promising, renewable and clean strategy.[1-3] TiO$_2$ as a classical semiconductor photocatalyst has been widely studied, however, only a small fraction of the solar spectrum (< 420nm) can be utilized by TiO$_2$ for its wide band gap (3.2 eV). Thus, the shift of the light response range of photoanode materials to visible light and the improvement of the quantum efficiency are important for the wide application of a photoelectrode.[4] Due to the visible light response, the metal oxide materials with narrower bandgaps have been studied intensively as photoanodes.[5,6] Hematite (α-Fe$_2$O$_3$) with a narrow band gap of 2.0~2.2 eV and favorable band position has gained significant attraction and been a promising material, also for its non-toxicity, low cost, natural abundance and electrochemical stability.[7] However, the reported water splitting efficiencies of hematite photoelectrodes are much lower for a number of disadvantages such as slow charge carrier mobility and fast electron-hole recombination rate. Among the synthesis techniques[8-17], hydrothermal method which eases operating and good crystallinity is a facile method to synthesize hematite photoelectrodes to improve the photoelectrochemical performance.

There are also some methods to improve the photoelectrochemical performance, such as surface modification[18] and morphology modulation[19]. In recent years, by removing the surface recombination center, the surface pretreatment by electrochemical cyclic voltammetry (CV) in the dark is expected as a universal way to increase the photoelectrochemical performances of the photoelectrode[20,21]. In the present study, the photoelectrochemical performances of the hematite photoanodes were analyzed with changing preparation conditions and the preparation conditions for the
calcination temperatures were optimized. After the electrochemical surface pretreatment, the hematite photoanode exhibits improved photoelectrochemical performance and the possible mechanism was also discussed.

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. The surfactant was purchased from Aldrich and used as received without further purification.

2.2. Synthesis of α-Fe$_2$O$_3$ photoanode

In the typical process, 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. The reaction solution with FeCl$_3$·6H$_2$O (1.6217 g) and surfactant in deionized water was transferred into the Teflon-lined stainless steel autoclave. The autoclave was sealed, heated and kept for different time.

2.3. 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, an Ag/AgCl electrode as the reference electrode and a high purity Pt foil as the counter electrode. The photocurrents of water oxidation were measured in 1 M KOH aqueous solution with a scan rate of 20 mV·s$^{-1}$. The electrochemical pretreatment was carried out as follows before the photoelectrochemical properties of the samples were measured.[20] The as-prepared sample was scanned by cyclic voltammetry for 30 cycles in 1 M KOH in the dark. The cyclic voltammetry scans were performed at the scan speed of 20 mV·s$^{-1}$ and with threshold reduction potential. A solar simulator was used as light source for photoelectrochemical measurement.

3. Results and Discussion

The influence of reaction time on the photo-electrochemical property of hematite samples through hydrothermal route after surface pretreatment is also investigated. Photocurrent curves of the hematite samples prepared at 180 °C for different time through hydrothermal route are shown in Fig. 1. When the hydrothermal reaction time is increased from 2 h min to 3 h, the photocurrent obviously decreases. The crystal size of the hematite sample grows with the increase of hydrothermal reaction time, which may be due to the easier recombination of photo-generated carriers. Thus, proper hydrothermal reaction temperature and time are crucial to obtain high photo-electrochemical performance.
Fig. 1 Photocurrent curves of $\alpha$-Fe$_2$O$_3$ samples prepared at 180 °C for different time, a. 2 h; b. 2.5 h; c. 3 h.

The photocurrent curves of hematite films before and after surface pretreatment are shown in Fig. 2. Compared with the hematite sample without electrochemical pretreatment, it is shown from Fig. 2 that the sample after the pretreatment shows the obvious enhancement of photocurrent. The electrochemical pretreatment makes the photocurrent of the hematite sample 1.3 times more than that of the sample without surface pretreatment at 0.4 V vs. Ag/AgCl. It has been previously reported that associated physically with the partial transformation of hematite, electrochemical reduction pretreatment can cause a favorable photohole transfer and a significant decrease of charge recombination [20]. From the above results, it is proven that the electrochemical pretreatment is also an efficient method to improve the photocurrent of the as-prepared hematite sample prepared by hydrothermal method.

Fig. 2 Photocurrent curves of the $\alpha$-Fe$_2$O$_3$ sample prepared at 180°C for 2 h, a. before surface pretreatment; b. after surface pretreatment.
As shown in Fig. 3, Fig. 4 and Fig. 5, low and high-resolution SEM images of the as-prepared hematite film prepared by the hydrothermal method for different time are measured. From the SEM images, it can be observed that the planar surface structure of the as-prepared hematite film prepared by the hydrothermal method for 2 h is compact and no obvious cracks appear. Thus, through hydrothermal method, the compact hematite films can be prepared. And with the increasing hydrothermal reaction time, the particles on the surface of the as-prepared hematite films which can be observed by SEM images. The bigger particle size may influence the photo-electrochemical efficiency of the as-prepared hematite film prepared by the hydrothermal method.

**Fig. 3** SEM image of the surface of hematite film prepared by hydrothermal method for 2h.

**Fig. 4** SEM image of the surface of hematite film prepared by hydrothermal method for 2.5h.
Fig. 5 SEM image of the surface of hematite film prepared by hydrothermal method for 3h.

4. Summary
In summary, to improve the photoelectrochemical performances of the hematite photoanode, the preparation conditions were optimized. The electrochemical surface pretreatment can improve the photoelectrochemical response of the hematite thin films, which is attributed to the favorable photohole transfer and the reduced electron–hole recombination.

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