Study of the stability of the iron oxide photoelectrode prepared through hydrothermal method

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Abstract. Iron oxide photoanode was obtained through hydrothermal method. The morphology of the hematite photoanode was investigated by scanning electron microscopy (SEM) and the photo-electrochemical stability performance was also evaluated. The photochemical stability of a photoelectrode is crucial point for practical application of a photoelectrochemical cell. The photoelectrochemical stability of hematite photoanode can be improved by the synthesis method.

Keywords: stability, photoelectrode, iron oxide.

1. Introduction

As photoanodes, the metal oxide materials with narrower bandgaps have been intensively studied due to the visible light response, and with a narrow band gap and favorable band position, hematite has gained significant attraction and also for its non-toxicity, low cost, natural abundance and electrochemical stability, it has been a promising material.[1-3]

A suitable synthesis method is also crucial for the hematite photoelectrodes to realize the high PEC performance with the application in a large scale by improving the stability of photoelectrode and reducing the electron-hole recombination and improve the electronic transport properties in hematite. Recently, for preparing hematite photoelectrodes, various preparation methods have been reported [4-13].

With a wide range of applications, hematite represents one of the most important iron oxides, including catalysts, rechargeable lithium batteries, gas sensors, nonlinear optics, and so on. For various atom densities in their hematite structure, the catalytic activities are different thus physical and chemical properties are found to be intensely sensitive to the size and shape of inorganic nanomaterials. Combined functionality with low cost, stability and corrosion-resistance, nontoxicity, it has been studied extensively. Thus, the fabrication of hematite with well-controlled size and shape has attracted considerable interest. [14-21]

Recently, synthesis studies have mainly focused on the modulation of the iron oxides’ morphologies, such as nanobelts, urchinlike, nanowires, nanotubes, nano/microrings, dendritic structures, peanutlike, nanocubes, shuttlelike, micropines, nanoflowers, cantaloupe-like, nanorods, [22-36] and so on. Iron oxides have been prepared via vapor-phase methods (physical and chemical processes), thermal...
decomposition of organometallic compounds, template methods (“soft” or “hard” template), and a series of wet chemical methods (including coprecipitation, solvothermal method, sol-gel, hydrothermal process, and so on). Among these methods, in all the wet chemical methods mentioned above, due to some advantages, including simple manipulation, mild synthetic conditions, and good crystallization of the products, the hydrothermal or solvothermal process is often used. With controlled size from microparticles to nanoparticles, less attention has been paid to the synthesis of monodisperse particles, although by Matijevic’s group, the fabrication of monodisperse magnetic particles have been pioneered in the early 1980s.[37] To meet the increasing technological demand, the controllable synthesis of dispersed micro/nanoparticles still needs to be greatly explored.

Furthermore, owing to its use in water treatment, hematite has attracted increasing interest. In both the trivalent form and hexavalent form, chromium present in aqueous system, has been placed on the top of the priority list of toxic pollutants by the USEPA. To living organisms, compared with trivalent form, hexavalent form with its higher solubility in water contaminated by steel manufacturing, electroplating, dyeing and etc., is more harmful [38-39]. Thus, the removal of pollutant ions in contaminated water is of great importance.

Over a wide pH range and the effectiveness, iron oxide-based materials have been paid attention to due to their chemical stability, selectiveness in the removal. The growth mechanism of iron oxides and modulation mechanism are usually investigated and the removal capacities of the as-prepared iron oxides are also measured.

While, as a facile method for synthesizing hematite photoelectrodes, hydrothermal method for its easy operating and good crystallinity is to improve the photoelectrochemical stability performance among the synthesis techniques. In the present study, by the hydrothermal method, hematite photoanode was prepared. The photoelectrochemical stability performances of the hematite photoanodes were also analyzed.

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 α-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 was transferred into the Teflon-lined stainless steel autoclave. The autoclave was sealed, heated at different temperatures and kept for different time. The as-prepared α-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

The morphologies of the as-prepared samples were characterized by field emission scanning electron microscopy (FESEM, JEOL JSM-7600F) with an electron accelerating voltage of 20 kV.

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, 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$^{-1}$. 

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3. Results and Discussion
Low and high-resolution SEM images of the as-prepared hematite film prepared by the hydrothermal method is shown in Fig. 1 and Fig. 2. From the SEM images, it can be observed that the planar surface structure of hematite is compact and no obvious cracks appear, which is shown that the compact hematite films can be obtained through hydrothermal method. Furthermore, even after the scrapping action, the hematite film also showed the adhesive property to the FTO substrate, and no changes were observed for the surface morphology of the hematite films after electrochemical measurements.

![Fig. 1 SEM image of the surface of hematite film prepared by hydrothermal method.](image1)

![Fig. 2 High-resolution SEM image of the surface of hematite film prepared by hydrothermal method.](image2)

The stability of the photocurrent after the surface pretreatment should be investigated because the photochemical stability of a photoelectrode is another crucial point for practical application of a photoelectrochemical cell. The photocurrent–time (i–t) curve of α-Fe₂O₃ sample after surface pretreatment in 1 M KOH aqueous solution is shown in Fig. 7. The photocurrent of α-Fe₂O₃ is initially
about 0.033 mA·cm\(^2\) and decreases to about 0.028 mA·cm\(^2\) after 120 min of illumination, and extremely low surface corrosion may induce the reduction of photocurrent during illumination[40]. The photocurrent of \(\alpha\)-Fe\(_2\)O\(_3\) only decreases to about 84% in air after 5000s. To further demonstrate the photostability of the \(\alpha\)-Fe\(_2\)O\(_3\) photoanode in 1 M KOH aqueous solution, the XRD patterns of the \(\alpha\)-Fe\(_2\)O\(_3\) samples before and after illumination was also investigate, and the result suggests that the \(\alpha\)-Fe\(_2\)O\(_3\) photoanode is assumed to be stable in 1 M KOH aqueous solution for 5000s.

![Fig. 3 Chronoamperometry (i–t) curve of hematite sample electrode in a 1 M KOH aqueous solution;](image)

### 4. Conclusions

In summary, by hydrothermal method, hematite thin films were deposited. The preparation conditions were optimized to increase the photoelectrochemical stability performances of the hematite photoanode. And the measurement results suggest that the \(\alpha\)-Fe\(_2\)O\(_3\) photoanode is assumed to be stable in 1 M KOH aqueous solution for 5000s.

### Acknowledgments

This work was financially supported by Natural Science Research Projects of Universities in Jiangsu Province (19KJB610014) and a grant from Scientific Research Project of Nanjing Vocational Institute of Transport Technology (JZ1912) and High-level Scientific Research Foundation for the Introduction of Talent of Nanjing Vocational Institute of Transport Technology.

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