

Thickness effect of hematite nanostructures prepared by hydrothermal method for solar water splitting



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ABSTRACT

Hematite nanostructures with various thicknesses were prepared for solar water splitting by controlling the HCl concentration in hydrothermal process. Results show that when the thickness increases, hematite will form layered structure on the substrate instead of the continuing growth of nanorods. A single layer of vertical nanorods shows the best performance for solar water splitting while multi-layers of nanorods show worse performance, which can be attributed to bad conductivity between hematite layers revealed by Mott–Schottky plots. Data clearly demonstrate the thickness effect of hematite nanostructures, which can be a key role for the performance of solar water splitting.

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1. Introduction

Hematite was recently considered to be a good photocatalyst for efficient solar water splitting due to its favorable optical band gap (2.1–2.2 eV), extraordinary chemical stability in oxidative environment, abundance, and low cost [1–10]. However, the practical performance of hematite for solar water splitting is far away from their theoretical prediction. Several factors were found to limit the performance of hematite such as poor conductivity, short lifetime of the excited-state carrier (10^{-12} s), poor oxygen evolution reaction (OER) kinetics, short hole diffusion length (2–4 nm), and improper band position for unassisted water splitting [5–10].

To explore hematite structures with excellent performance for solar water splitting, various methods have been used to prepare hematite such as spray pyrolysis [11], sol–gel [12], hydrothermal [6], and atmosphere pressure chemical vapor deposition (APCVD) [9]. Among all these methods, hydrothermal process was reported to be an effective way to prepare highly efficient hematite nanostructures [6,8,10,13–15]. The pristine hematite nanostructures prepared by typical hydrothermal method can easily achieve a relatively high performance, which is a good start for further treatment such as doping, annealing or surface treatments to obtain better performance [6,10,15]. Recently, by coupling Pt-doping and Co–Pi catalysts to pristine hematite prepared by hydrothermal

method, a record-breaking photocurrent of 4.32 mA/cm² at 1.23 V vs. reversible hydrogen electrode (RHE) was achieved [10]. The work also showed the important role of pristine hematite as a good starting material for further modification to achieve high performance [10]. Although hydrothermal method has been widely used to prepare hematite nanostructures, the detailed synthesis process and various factors which may affect the performance of final products in hydrothermal method are still unclear. It is thus important to investigate various influence factors in hydrothermal process as a fundamental study which will benefit the future application. Here we find that the HCl concentration may significantly affect the thickness of hematite nanostructures and then affect the performance for solar water splitting. Results show that when the thickness increases, hematite will form layered structure on the substrate instead of the continuing growth of nanorods. Interestingly, a single layer of vertical nanorods shows the best performance for solar water splitting while multi-layers of nanorods show worse performance, which can be attributed to bad conductivity between hematite layers. Data clearly reveal the thickness effect of hematite nanostructures in hydrothermal process for the performance of solar water splitting and may help to understand other solution process for the preparation of hematite nanostructures.

2. Experimental

2.1. Preparation of α -Fe₂O₃ photoanodes

Hematite nanostructures were prepared on a fluorine-doped SnO₂ (FTO, Nippon Sheet Glass, Japan, 14 ohm/sq) glass by a

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hydrothermal method [6]. A teflon-lined stainless steel autoclave was filled with 60 ml aqueous solution containing 0.15 M of ferric chloride ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$, Sinopharm Chemical Reagent Co., Ltd.), 1 M sodium nitrate (NaNO_3 , Sinopharm Chemical Reagent Co., Ltd.) and various amounts (0, 60, 120, 180, 240, 330 μl) of HCl (45.3–45.8 wt%). The FTO glass was cleaned with acetone, ethanol and deionized water. The cleaned FTO glass slide (60 mm \times 35 mm \times 2 mm) was put into the autoclave and heated at 95 $^\circ\text{C}$ for 4 h. The resulted samples were mainly yellow color film (FeOOH) (except for the sample with 330 μl HCl which showed white color) formed on the FTO substrate. The samples treated with various amounts (0, 60, 120, 180, 240, 330 μl) of HCl were labeled as A₁, B₁, C₁, D₁, E₁ and F₁, respectively. Then the samples were washed with deionized water and cut into 17.5 mm \times 10 mm \times 2 mm pieces for further annealing treatment. The samples were sintered in air at 550 $^\circ\text{C}$ for 2 h and annealed at 800 $^\circ\text{C}$ for additional 5 min for photoelectrochemical (PEC) measurements. The final samples were labeled as A, B, C, D, E and F, respectively.

2.2. Structural characterization

The scanning electron microscopy (SEM) images of hematite nanostructures were taken on a FEI-quanta 200 scanning electron microscope with acceleration voltage of 20 kV. Transmission electron microscopy (TEM) was obtained with a FEI/Philips Techai 12 BioTWIN transmission electron microscope. X-ray Diffraction (XRD, PANalytical, Zmpyrean) was also used for structural characterization.

2.3. PEC measurements

Hematite photoanodes on FTO substrate were covered by non-conductive hysol epoxy except for a working area of 0.1 cm^2 . All PEC measurements were carried out using CHI 660D electrochemical workstation in a three-electrode electrochemical cell with a Pt wire as a counter electrode and an Ag/AgCl electrode as a reference. The Electrolyte was an aqueous solution of NaOH with a pH of about 13.6, bubbled with N_2 for 20 min before measurement. The measured voltage was converted into the potential vs. reversible hydrogen electrode (RHE). In a typical experiment, the potential was swept from 0.7 V to 1.8 V vs. RHE at a scan rate of 50 mV s^{-1} . Xenon High Brightness Cold Light Sources (XD-300) coupled with a filter (AM 1.5G) were used as the white light source and the light power density of 100 mW cm^{-2} (spectrally corrected) was measured with a power meter (Newport, 842-PE). Capacitance was derived from the electrochemical impedance obtained at each potential with 10,000 Hz frequency in the dark. Mott–Schottky plots were generated from the capacitance values.

3. Results and discussion

Fig. 1 shows the PEC performance of samples A–F. PEC measurements were performed in 1 M NaOH electrolyte (pH about 13.6) using a three-electrode electrochemical cell with hematite nanostructures on FTO as the working electrode, a platinum coil as the counter electrode, and a reference of Ag/AgCl. The photocurrent density–applied potential (J – V) scans for hematite nanostructures were measured with the AM 1.5G simulated solar light at 100 mW/cm^2 . In Fig. 1 we show a comparison of the J – V scans for samples A–F prepared with various amounts of HCl. Sample A without HCl (black curve) shows a photocurrent of 0.51 mA/cm^2 at 1.23 V vs. RHE. When the amount of HCl increases, hematite samples B–E show enhanced performance than that for sample A, until in sample F the amount of HCl is too much preventing the growth of

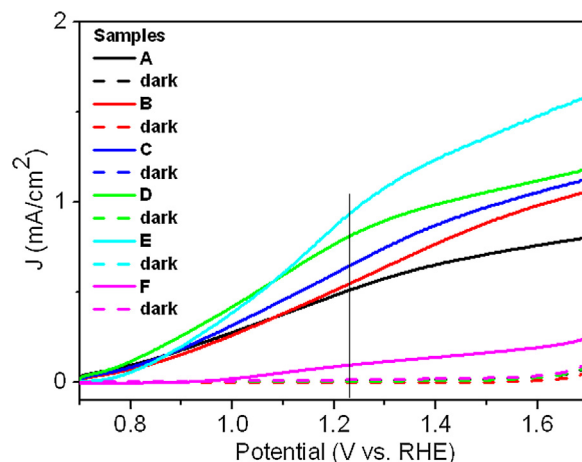
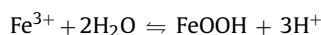


Fig. 1. J – V scans for hematite samples A–F.

hematite nanostructures. Especially, sample E shows the best performance with a photocurrent of 0.94 mA/cm^2 at 1.23 V vs. RHE, which is almost two times over that for sample A without HCl. When preparing hematite nanostructures in hydrothermal process, the reaction can be simply described as below:



The increase of H^+ in solution may reduce the formation of FeOOH . Thus the concentration of HCl will influence the thickness of FeOOH deposited on FTO substrate, which may significantly affect the PEC performance of final hematite samples. Sample E shows the best performance indicating an optimized HCl concentration in hydrothermal process.

To understand the performance evolution of hematite nanostructures prepared with various amounts of HCl, we show the SEM images of samples A, E and F in Fig. 2. The samples for FeOOH structure before annealing (A₁, E₁ and F₁) are also shown for comparison. For samples A and E, the samples before and after annealing show similar morphology but the nanostructures after annealing show slightly increased size. Both samples A and E after annealing show structures with mainly vertical nanorods deposited on the FTO substrate, which is in good agreement with previous reports using similar synthesis method [10,14]. However, sample E shows a uniform distribution of nanorods covering the FTO substrate while the nanorods in sample A tend to assemble as isolated islands. The morphology difference between sample A and sample E revealed by SEM images could be related to the different PEC performance, which need to be further addressed. For sample F, SEM image shows that almost no hematite nanostructures can be observed and the surface is very similar to the FTO substrate, which is consistent with the PEC performance. XRD data for samples A, E, F and FTO substrate are also shown in Fig. 3. The XRD data for samples A and E can be indexed to the characteristic peaks of typical hematite structure (JCPDS 33-0664) after subtracting the peaks from the FTO substrate, while sample F shows similar peaks to that of FTO substrate.

In Fig. 4 the SEM cross-section images of hematite photoanodes (A and E) have been shown to reveal the relationship between the concentration of HCl and the morphology of the resulted hematite nanostructures. The bottom solid film about 340 nm in both images is FTO conductive layer, while the materials on the conductive film are hematite nanorods. For sample E the hematite nanostructures are randomly deposited on the conductive film showing some vertical nanorods, which is consistent with the top view SEM image in Fig. 2. However, for sample A, a thick hematite

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