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Facile Hydrothermal Synthesis of Three Dimensional Hematite Nanostructures with Enhanced Water Splitting Performance

Mingyang Li, Ziyang Zhang, Feiyi Lyu, Xinjun He, Zhihao Liang,
Muhammad-Sadeeq Balogun, Xihong Lu, Ping-Ping Fang*, Yexiang Tong*

KLGHEI of Environment and Energy Chemistry, MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Guangzhou 510275, China

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ABSTRACT

Hematite (α-Fe_2O_3) photoanodes has received considerable attention to produce hydrogen and oxygen by the photoelectrochemical (PEC) reaction due to its chemical stability, appropriate band and abundance. Although various sizes and morphologies of α-Fe_2O_3 had been synthesized to enhance the photoanode performance, their photoactivity is still unsatisfactory for their inefficient charge transfer or light harvesting. In this work, we utilized a facile hydrothermal method to tune the size and morphology of the α-Fe_2O_3 nanostructures by simply controlling the reaction temperature, and found that the 500 nm 3D nanospheres (NSs) exhibit highest catalytic activity for the PEC water splitting. We systematically studied the morphology and growth mechanism of α-Fe_2O_3 nanorods (NRs) and NSs, and found the temperature can greatly influence the final morphology. In comparison to 1D NRs, the 3D NSs can make the PEC activity enhanced for five times due to the optimal charge transfer and light harvesting. This report provides a new insight on the relationships between nanostructures and photoanode performances, and can be applied in other PEC water splitting materials.

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1. Introduction

Due to the increasing energy demands and growing environmental concerns, efficient utilization of the solar energy has become a crucial way to solve these issues. Photoelectrochemistry is emerging as a promising way to store the intermittent solar energy into molecular O_2 and H_2 via photoelectrodes [1–3]. Since the innovative research of Fujishima in TiO_2 photoelectrodes [4], extensive studies have been reported in finding appropriate nanomaterials enhance the catalytic activity for the photoelectrochemical (PEC) hydrogen evolution [5–7]. Among various semiconductors, hematite (α-Fe_2O_3) has been considered as a promising material for PEC H_2 evolution because of its low cost, abundance, nontoxicity and favorable bandgap (2.2 eV) [8–11]. In spite of these merits, the photoanode performance of α-Fe_2O_3 is yet unsatisfying due to its short charge diffusion length, high recombination losses and low absorption coefficient [12–17]. Therefore, it is very important to find efficient and simple ways to solve these problems and enhance the photoactivity.

1D-nanos``tructured α-Fe_2O_3, such as nanowires arrays [12,13], nanorods (NRs) arrays [14,16] and nanotubes arrays [15,17] have been prepared to resolve the intrinsic drawbacks of α-Fe_2O_3 for PEC water splitting. Compared to its bulk counterparts, 1D morphology can facilitate the charge diffusion and decrease excess combination loss, and thus enhances the PEC water splitting performance of α-Fe_2O_3. For instance, Wang et al. fabricated the silicon core α-Fe_2O_3 shell NRAs on silicon substrate by the metal-catalyzed electroless etching method [12]. Ling et al. synthesized α-Fe_2O_3 nanowires arrays by the hydrothermal method [13]. Hou et al. also reported the branched α-Fe_2O_3 NRs arrays by a hydrothermal deposition on Ti mesh [14]. The 1D nanostructures have high PEC water splitting performances because the short diffusion distances for the photogenerated minority carriers were alleviated [12–17]. However, these methods often lead to unsatisfying performances or require undesirable operating conditions, such as a complicated substrate and tedious steps. In addition, the inefficient utilization of light in the 1D morphology is a great problem for the PEC water splitting performance. Few investigations have focused on overcoming the inefficient light absorption of α-Fe_2O_3 nanostructures to enhance the light harvesting. Recently, great efforts have been devoted to prepare 3D nanospheres (NSs) of TiO_2 [18,19] and $BiVO_4$ [5], which have strong light scattering and enhance the light-harvesting efficiency

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* Corresponding authors. Tel.: +86 20 84110071; fax.: +86 20 84112245.
E-mail addresses: fangpp3@mail.sysu.edu.cn (P.-P. Fang), chedhx@mail.sysu.edu.cn (Y. Tong).

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in a broad wavelength range. For example, Wu et al. have found that the hierarchical TiO_2 NSs possess exceptional light harvesting efficiency originated from the large sized light scattering [18,19]. Kim et al. also have reported that 3D $BiVO_4$ nanoporous exhibit significant performances of solar water splitting because of the increased light harvesting efficiency [5]. Inspired by these investigations and notable results, it is well worth preparing 3D α-Fe_2O_3 NSs with suitable diameter by simple and facile methods to improve the light harvesting and enhance the PEC water splitting performance.

Herein, we utilized a facile and cost-effective hydrothermal method to synthesize high photoanode performance α-Fe_2O_3 nanostructures with different sizes and morphologies by varying the hydrothermal temperatures. We first synthesized the akaganeite (β-FeOOH) at different temperature to control the size and morphology of the β-FeOOH nanostructures, and then annealed the samples at 750 °C to get the α-Fe_2O_3 without changing the size and morphology. The α-Fe_2O_3 nanostructures with different sizes and morphologies were obtained and systematically investigated in the PEC water splitting applications.

2. Experimental Section

2.1. Preparation of α-Fe_2O_3 nanostructures

The α-Fe_2O_3 was prepared on a fluorine-doped tin oxide coated glass (FTO) substrate based on a hydrothermal method reported elsewhere [13]. A Teflon-lined stainless steel autoclave of 25 mL capacity was filled with 20 mL aqueous solution containing 0.15 M of $FeCl_3$ and 1 M $NaNO_3$ at pH 1.5 (adjusted by HCl). A piece of FTO glass slide (2 cm × 3 cm), washed with acetone, ethanol, and then deionized water, was put into the autoclave, then heated at 100, 120, 140, 160 and 180 °C for 5 h in an oven and naturally cooled down to ambient temperature, respectively. Finally, a uniform layer of β-FeOOH on the FTO substrate was obtained. The akaganeite-coated substrate was then washed with deionized water and subsequently sintered in air at 750 °C for 30 min in a furnace. After the annealing process at 750 °C for 30 min, the β-FeOOH was converted into α-Fe_2O_3 and the testing area of α-Fe_2O_3 was tailored into 1 cm × 1 cm to perform the photoelectrochemical water splitting measurements. Detail can be seen in the S1 in the Supporting Information (SI).

2.2. Characterization methods

The samples were characterized by field emission scanning electron microscope (FE-SEM, JSM-6330F), X-ray Diffractometer (XRD, D-MAX 2200 VPC), and X-ray Photoelectron Spectroscopy (XPS, ESCALab 250). The powder sample scraped from the FTO substrate was test by Transmission electron microscopy (TEM, JEM 2010-HR). The UV–vis spectra of the samples on the FTO were measured with a UV-Vis-NIR Spectrophotometer (UV-Vis, Shimadzu UV-2450). Electrochemical surface area was determined from double layer capacitance measurements. Cyclic voltammetry (CV) was performed in the region between 0.1 and 0.4 V vs. Ag/AgCl in 0.1 M KOH conducted in the dark. CVs were obtained for a potential range in which no faradic processes were occurring, and the geometric current density at a specified potential was plotted against the scan rate of the CV. The active surface area has a linearity with the double layer capacitance, which is equal to the slope of current density *vs.*scan rate, therefore, we use this method to characterize the active surface area and do the normalization according to the literature [10,20,21].

2.3. Photoelectrochemical water splitting measurements

PEC water splitting measurements of the α-Fe_2O_3 photoanodes were conducted in a three-electrode electrochemical cell, using a Pt foil as a counter electrode and an Ag/AgCl electrode as a reference electrode, respectively. An aqueous solution of 1 M NaOH with a pH 13.6 was regarded as the electrolyte. All linear sweep voltammograms (LSV) were measured by a CHI 760D electrochemical workstation under illuminating from the front side by a solar simulator (Newport 6255, 150 W) with a power density of 100 mW/cm^2. Incident-photo-to-current-efficiencies (IPCE) were measured with a xenon lamp (Newport 69911, 300 W) coupled with a monochromator (Oriel Cornerstone 260 1/4m).

3. Result and Discussion

The α-Fe_2O_3 photoanodes were synthesized using a hydrothermal deposition method. The experimental details are shown in experiment section. We first synthesized β-FeOOH at 100 °C by hydrothermal deposition method in 20 mL aqueous solution containing 0.15 M of $FeCl_3$ and 1 M $NaNO_3$ at pH 1.5, and the

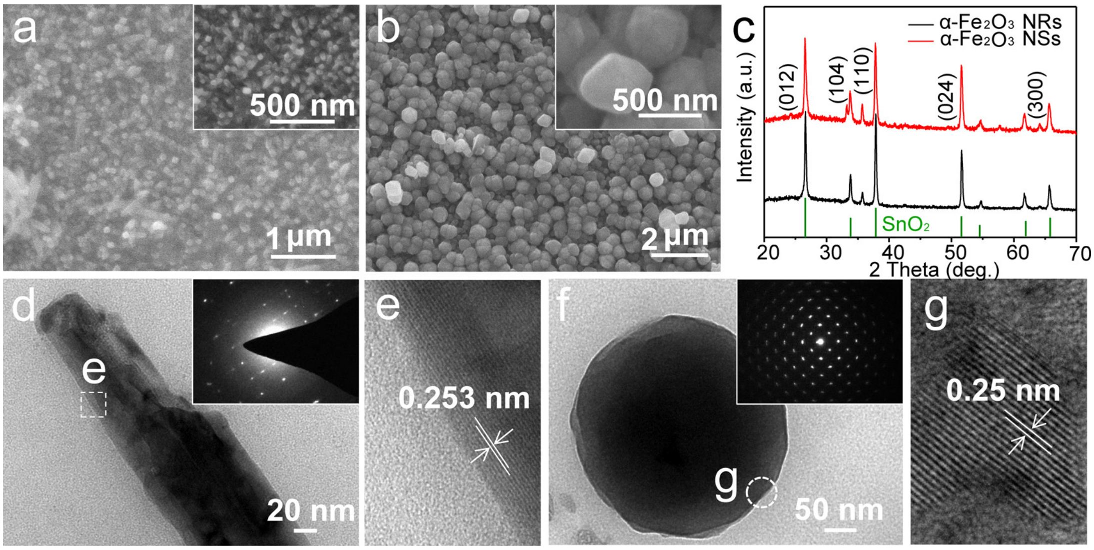

Fig. 1. SEM images of (a) α-Fe_2O_3 NRs and (b) α-Fe_2O_3 NSs; inset: magnified SEM of α-Fe_2O_3 NRs and α-Fe_2O_3 NSs; (c) XRD spectra of α-Fe_2O_3 NRs and α-Fe_2O_3 NSs; (d) TEM and (e) HRTEM images of α-Fe_2O_3 NRs; (f) TEM and (g) HRTEM images of α-Fe_2O_3 NSs.

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