Enhanced efficiency of hematite photoanode for water splitting with the doping of Ge

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ABSTRACT

Ge doped α-Fe$_2$O$_3$ nanowires are synthesized through a hydrothermal procedure with GeO$_2$ as a precursor and investigated as photoanodes for water splitting. The content of Ge in the photoanode rises with the increase of the amount of GeO$_2$ in the precursor solution. A proper amount of Ge facilities the preferred oriented growth of the (110) plane of α-Fe$_2$O$_3$, while excessive Ge hinders the growth of α-Fe$_2$O$_3$ crystals. The doping of Ge increases the absorption efficiency and decreases the recombining rate of the photogenerated electrons and holes. Ge also improves the density and transfer rate of the charge carriers in the photoanode. Ge doped α-Fe$_2$O$_3$ photoanode exhibits a highest photocurrent density of 0.92 mA cm^{-2} at 1.23 V vs. reversible hydrogen electrode under AM 1.5 G simulated sunlight, which is nearly twice of that obtained by pure α-Fe$_2$O$_3$ under the same condition.

Introduction

The exploitation and consumption of fossil fuels contribute a lot to the rapid development of the global economy, but also result in an increasing risk of energy shortage and environmental pollution problems [1]. The conversion and utilization of sustainable solar energy is one of the solutions to these problems. Meanwhile, hydrogen is regarded as the most promising energy substitute in the future due to its high heat value and super clean nature [2,3,4]. In 1972, Fujishima and Honda [5] found that water can split into hydrogen and oxygen under simulated solar light on a TiO$_2$ semiconductor. Since then, more semiconductor with high photoelectric activity had been explored [6], and photoelectrochemical (PEC) water splitting has been regarded as an ideal approach to resolve the environmental issues and energy crisis and extensively studied all around the world [7].

A PEC cell is constituted by a photoanode and a photocathode for the evolution of oxygen and hydrogen,

respectively. Hematite (α-Fe$_2$O$_3$) has been found as one of the most promising photoanode materials due to its suitable band gap of 2.0–2.2 eV, which is able to absorb 40% of solar spectrum [8,9,10]. Hematite is the most thermodynamically stable form of iron oxide, and it is abundant and inexpensive [11,12,13,14]. Zhang et al. [15] synthesized P-doped hematite photoanodes by a impregnation method, and a current density of 3.1 mA cm^{-2} is obtained at 1.23 V vs. reversible hydrogen electrode (RHE). However, there are still drawbacks of hematite those restrict the PEC performance, such as short hole diffusion length (2–4 nm) [16,17], poor oxygen evolution reaction kinetics [11,18], short excited-state lifetime (~10^{-12} s) [19,20] and low absorptivity [21]. Due to these disadvantages, the experimental energy conversion efficiency of PEC cells with hematite photoanodes is far below its theoretical value of 12.9% [22].

Morphology control and element doping are two of the most common strategies to enhance the PEC performance of hematite photoanodes [23]. The former is to fabricate photoanodes with suitable nanostructure and scale, while the latter is usually used to enhance the electrical conductivity and modify the band structure of photoanodes [24]. Appropriate doping of foreign elements can improve the mobility of charge carriers and promote the dispersion of photogenerated holes. It has been reported that Si and Sn doped hematite showed outstanding photoelectrochemical performance [19,25,26,27,28]. The tetravalent dopants act as electron donors, resulting in the improvement of the electrical conductivity. Compared with Si and Sn, Ge exhibits a high solubility in α-Fe$_2$O$_3$ [23,29,30,31,32]. Meanwhile, Ge has a guiding effect on the growth of α-Fe$_2$O$_3$ crystal within (001) basal plane which shows a high electrical conductivity [33,34]. Therefore, Ge is considered as a promising dopant in α-Fe$_2$O$_3$ and has drawn much attention in recent years [29].

Ge doped hematite has been synthesized through various approaches such as sputter deposition, spray pyrolysis, hydrothermal method, dip-coating and ultrasonic decomposition [23,31,33,35,36]. Among these methods, the hydrothermal technology is an efficient way to fabricate single-crystal nanorods or nanowires of α-Fe$_2$O$_3$ which facilitate electron transport and surface reaction. Liu et al. [33] synthesized Ge-doped hematite nanosheets through a hydrothermal process and obtained a photocurrent density of 1.4 mA cm^{-2} at 1.23 V vs. RHE. However, Ge colloidal solutions prepared with pulse lasers are used as precursors during the hydrothermal procedure [33,36], which is expensive and time consuming for large-scale applications. In this work, Ge doped α-Fe$_2$O$_3$ is synthesized through a simplified hydrothermal approach with GeO$_2$ as a precursor instead of Ge colloidal solution. The effects of the doping amount of Ge on the photoelectrochemical properties of α-Fe$_2$O$_3$ photoanode are investigated.

Experimental

Materials preparation

α-Fe$_2$O$_3$ nanowires grown on a fluorine-doped tin oxide (FTO) substrate were prepared through a hydrothermal procedure [16]. Briefly, the FTO coated glass substrate (20 × 10 mm^2) was cleaned with deionized water and ethyl alcohol for 15 min in an ultrasonic bath, respectively. 25 ml aqueous solution which consists of 0.21 g sodium nitrate (NaNO$_3$, 99.0%, Guangfu fine chemical, Ltd., China) and 0.608 g iron chloride hexahydrate (FeCl$_3$·6H$_2$O, 99%, Aladdin), with a pH of 1.4 adjusted with hydrochloric acid, was used as the precursor. The precursor was transferred to a 50 ml Teflon-lined stainless steel autoclave, and the FTO glass was immersed in the solution with an exposed area of 10 × 10 mm^2. The autoclave was sealed and kept at 100 °C in an oven for 10 h, and then cooled to room temperature. The obtained film was annealed at 550 °C for 2 h and further calcined at 800 °C for 20 min to get the α-Fe$_2$O$_3$.

Ge doped α-Fe$_2$O$_3$ samples were synthesized through a similar procedure with the addition of a certain amount of germanium dioxide (GeO$_2$, 99.9999%, Real&Lead Chemical Co., Ltd., China) in the precursor solution. The amounts of GeO$_2$ added were 0.0078, 0.0131, 0.0208 and 0.0261 g, which were equivalent to 3, 5, 8 and 10 mmol L^{-1}, respectively. The obtained Ge doped α-Fe$_2$O$_3$ photoanodes are referred to as Ge-3, Ge-5, Ge-8 and Ge-10, respectively.

Characterization

The surface properties of the pure and Ge-doped α-Fe$_2$O$_3$ films were analyzed with an ESCA PHI 1600 X-ray photoelectron spectrometer (XPS) with a Mg Kα X-ray excitation source. The elemental contents of the photoanodes and the solutions after the hydrothermal process were analyzed with an inductively coupled plasma optical emission spectrometer (ICP–OES, VISTA–MPX, Varian). The photoanode samples were dissolved in a HCl aqueous solution. The suspended solids in the solutions were centrifugal separated from the solution before the ICP test. X-ray diffraction (XRD) patterns of the samples were collected from 20° to 80° at a speed of 5° min^{-1} with a Bruker AXS, D8–S4 powder diffractometer with Cu Kα illumination (40 kV × 200 mA). The morphologies of pure and Ge-doped α-Fe$_2$O$_3$ films were observed with a Hitachi S-4800 field emission scanning electron microscope (SEM). The ultraviolet–visible (UV–Vis) diffuse reflection spectra were recorded using a PerkinElmer L750 spectrometer.

Photoelectrochemical measurements

The photoelectrochemical properties of the photoanodes were investigated using a three-electrode configuration with a Pt sheet (10 × 10 mm^2) as the counter electrode, Ag/AgCl in 3 mol L^{-1} KCl aqueous solution as the reference electrode and 1 mol L^{-1} NaOH aqueous solution (pH = 13.6) as the electrolyte. The anodes were illuminated from the reverse side of the FTO glass with a simulated sunlight from a 300 W xenon lamp (Perfect Light, PLS-SXE-300) using an AM 1.5 G filter. The intensity of the light was 100 mW cm^{-2}. The polarization curves of the photoanodes were recorded between 0.6 and 1.6 V vs. RHE at 10 mV s^{-1} with an electrochemical workstation (CHI 660B, CH Instrument, Austin, TX). The potential of the RHE is calculated with the Nernst equation (Eq. (1)).

$$E_{RHE}(V) = E_{Ag/AgCl}^{0}(V) + E_{Ag/AgCl}(V) + 0.059pH \qquad (1)$$

where $E_{Ag/AgCl}^{0}$ is 0.1976 V. Mott-Schottky (M-S) experiments were carried out at 50 mV s^{-1} under 1 kHz in the dark.