Enhanced photoelectrochemical performance of Ti-doped hematite thin films prepared by the sol–gel method

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ABSTRACT

Ti-doped α-Fe$_2$O$_3$ thin films were successfully prepared on FTO substrates by the sol–gel route. Hematite film was characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and energy dispersive spectrometer (EDS). The XRD data showed α-Fe$_2$O$_3$ had a preferred (1 1 0) orientation which belonged to the rhombohedral system. Interestingly, the grains turned into worm-like shape after annealed at high temperature. The IPCE could reach 32.6% at 400 nm without any additional potential vs. SCE. Titanium in the lattice can affect the photo electro chemical performance positively by increasing the conductivity of the thin film. So the excited electrons and holes could live longer, rather than recombining with each other rapidly as undoped hematite. And the efficient carrier density on the Ti-doped anode surface was higher than the undoped anode, which contribute to the well PEC performance.

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1. Introduction

Hydrogen energy is clean, sustainable and of vast storage on the earth. Searching for an environmental friendly and inexpensive way to produce hydrogen is still a key point to make this energy industrial available. The photocatalytic decomposition of water into H$_2$ and O$_2$ is a promising way [1]. In 1972, Honda and Fujishima first discovered that the n-type TiO$_2$ electrode could split water into H$_2$ and O$_2$ irradiated under ultraviolet light [2]. However, the titanium dioxide photocatalyst can only make use of the ultraviolet radiation, which occupies just 4% of the total solar energy. During several decades, many new photocatalysts had been developed [3–5], however, no really suitable one had been found, owing to all kinds of reasons (e.g. high electron–hole recombination, wide energy band gap, or low transfer efficiency) [6,7]. Water splitting is an up-hill reaction with ΔG = +237 kJ/mol, which means that a 1.23 V voltage is needed to split water in the ideal condition [8]. When a semiconductor is used to split water, it must have a proper band gap larger than 1.23 eV. So it can absorb most of the photons having the energy higher than the low limit and then excite electrons and holes to participate in the half reaction. Meanwhile, it should have a right conduction band position vs. E_{H^+/H_2}, so we can

get H$_2$ without additional driving energy. The most appropriate band gap should be greater than 1.8 eV due to the over potential when the electrode is immersed in the electrolyte. Some materials have the ideal band gap, e.g. CdS (2.4 eV) [9], but they are unstable and may cause photo-corrosion in the electrolyte when irradiated.

Hematite (α-Fe$_2$O$_3$) has received much attention because of its advantages (abundance, low cost, an appropriate band gap suitable for visible light, nontoxicity and electrochemical stability) [10]. A variety of synthetic methods have been used to prepare hematite films, such as magnetron sputtering, ultrasonic spray pyrolysis, sol–gel and electrochemical deposition [11–13]. However, the photoconversion efficiency of hematite thin films is still low because of its short carrier diffusion lengths, low absorption coefficient and high electron–hole recombination rate. Many methods have been investigated to improve the photo-electrochemical performance of hematite, including doping of Si, Mg, Sn, Zn, Pt, Al, Mo, Cr, Au, Ag [14–19]. Some of the results are attractive, e.g. the Si doped α-Fe$_2$O$_3$ thin films have the IPCE of 42% at 370 nm, measured in 1 M NaOH solution with the bias 1.43 V vs. NHE.

Recently, our group investigated the effect of doping with Ti on the properties of hematite thin films by sol–gel method. Compared with undoped hematite thin films, doping with Ti can improve the photoelectrochemical performance a lot. The key point is that there is no bias added to the working electrode – α-Fe$_2$O$_3$ thin film. As we know from other reports, this phenomenon is first reported by now.

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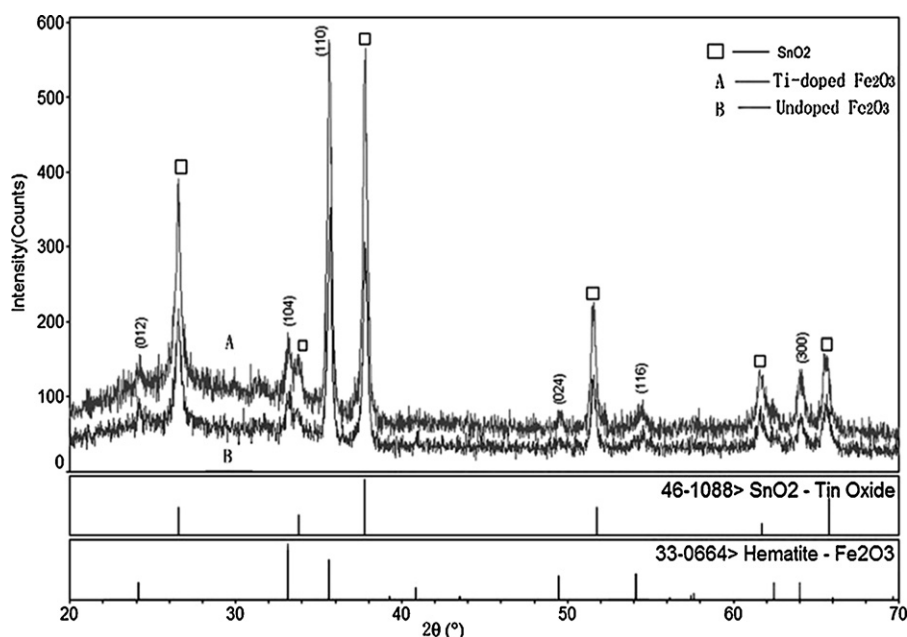*E-mail address:* rlwang26@yahoo.com.cn (R. Wang).

Fig. 1. XRD patterns of (A) Ti-doped hematite films (B) undoped hematite films on FTO substrates annealed in air for 3 h at 500 °C, the squares denote peaks from FTO substrates. Lines belonging to the hematite and tin oxide diffraction pattern are included.

2. Experiment

Hydrate ferric nitrate $Fe(NO_3)_3 \cdot 9H_2O$ (SIGMA-ALDRICH, 99.99%) was dissolved in a mixture of acetylacetone (SIGMA-ALDRICH, ≥99%), ethanol and polyvinylpyrrolidone (ALDRICH, AR). Then $C_{12}H_{28}O_4Ti$ (ACROS, 98%) was added into the mixture. After that, the solution was kept stirring at room temperature for 6 h. Thin films were grown on F-doped tin oxide (FTO, Nippon Sheet Glass Co., Ltd., 2.5 mm × 2.5 mm) substrates by spin coating, and then annealed at 500 °C for 2 h.

The structure of the films was studied by X-ray diffractometer (Dandong Fangyuan Instrument Co., Ltd./DX-2000) with the Cu Kα (λ = 1.54056 Å, at 40 kV and 25 mA). The scan scale 2θ was from 20° to 70° with a rate of 0.02°/s [20]. The X-ray photoelectron spectra (KRATOS, XSAM800) was measured at room temperature with Al Kα radiation source and the overall resolution was 0.8 eV [21]. The morphology and ingredient of the samples were characterized by scanning electron microscopy (HITACHI, S-4800) at 3 kV. The magnifications of top-view were 100 k and 200 k. The samples' optical properties were measured from a UV–visible spectrophotometer (Beijing Purkinje General Instrument Co., Ltd., TU-1900), the scan range varied from 400 nm to 650 nm with a 3 nm wavelength interval. The photoelectrochemical performances of samples were measured using a homemade three-electrode photoelectrochemical test system. The reactor was fitted with a quartz window, and the film was illuminated by a 150 W xenon arc lamp [22]. In the system, graphite-rod was used as the counter electrode, and a saturated calomel electrode (SCE) was used as the reference electrode respectively. All the tests were carried out in 1 M NaOH solution.

3. Results and discussions

3.1. X-ray diffraction (XRD)

X-ray diffraction (Fig. 1) shows α-Fe_2O_3 films have the rhombohedral lattice, with a preferential orientation of (1 1 0). It is reported that the orientation of α-Fe_2O_3 films was affected by the SnO_2 interfacial layer [23,24]. The unmarked peaks are the diffraction data of FTO layer. The intensity of the (1 1 0) peak increases largely after Ti

was doped into the film. Electrons in the bulk film have different drifting velocity along different lattice orientation. So, when the (1 1 0) direction dominates in the film, the electron can transport more easily than other directions [25]. It happened that Ti doping affects the orientation of the film. Further more, each Ti^{4+} ion can donor one free electron in the lattice, which can increase the conductivity of the thin film. The IPCE results in the later test just verified the two hypothesizes above.

3.2. X-ray photoelectron spectroscopy (XPS)

Table 1 presents (a) elements, area (CPS), sensitivity factor and atomic surface proportion of detected elements for the Ti-doped hematite catalyst; binding energy, area, FWHM and %GL of (b) Fe 2p (c) Ti 2p. Percentages (calculated using area (CPS) divided by sensitivity factor) of Fe, Ti and O are around 31.28%, 2.63% and 66.09%. Fig. 2 reveals that the Fe $2p_{3/2}$ and Ti 2p peaks are at 710.810 eV and 458.352 eV, respectively. The results indisputably prove the presence of Fe^{3+} and Ti^{4+} from the Ti-doped thin films refer to the table of element electron binding energy [26,27]. The binding energy of Ti 2p is 458.352 eV, while the standard binding energy of titanium

Table 1
(a) Elements, area (CPS), sensitivity factor and atomic surface proportion of detected elements for the Ti-doped hematite catalyst. (b) Binding energy, area, FWHM and %GL of Fe 2p. (c) Binding energy, area, FWHM and %GL of Ti 2p.

(a) Element	Area (CPS)	Sensitivity Factor	Percentage
Fe	37491.1	2	31.28%
Ti	1892.4	1.2	2.63%
O	26138.6	0.66	66.09%

(b) Peak (Fe2p)	Position	Area	FWHM	%GL
0	710.810 eV	29239.961	4.100 eV	80%
1	724.244 eV	17718.932	5.550 eV	80%
2	717.271 eV	8251.080	4.959 eV	80%

(c) Peak (Ti 2p)	Position	Area	FWHM	%GL
0	458.352 eV	1892.385	2.495 eV	80%
1	463.585 eV	1399.857	3.276 eV	80%