INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–10

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he

Significantly improve photoelectrochemical performance of Ti:Fe_2O_3 with CdSe modification and surface oxidation

Jinyun Xiong [a,c,1], Jiale Xie [b,1], Pingping Yang [a,b,c], Xiaorong Liang [a,c], Chang Ming Li [a,b,c,*]

[a] Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, PR China

[b] Institute of Materials Science and Devices, Suzhou University of Science and Technology, Suzhou 215009, PR China

[c] Chongqing Key Laboratory for Advanced Materials & Technologies of Clean Electrical Power Sources, Chongqing 400715, PR China

ARTICLE INFO

Article history:
Received 28 March 2018
Received in revised form
1 May 2018
Accepted 23 May 2018
Available online xxx

Keywords:
Photoelectrochemical water splitting
Hematite
Cadmium selenide
Stability
Surface oxidation

ABSTRACT

Significant interest has been arisen to explore photoanodes for full optical absorption spectrums and good stability in photoelectrochemistry. Herein CdSe is used to modify Ti:Fe_2O_3 photoanode forming Ti:Fe_2O_3/CdSe heterojunction. Combining with an air annealing treatment, Ti:Fe_2O_3/CdSe exhibits a 6.5 times higher photocurrent density that of the pristine Ti:Fe_2O_3 to achieve 3.25 mA cm^{-2} at 1.2 V vs. RHE. The photoelectrochemical (PEC) stability of Ti:Fe_2O_3/CdSe annealed in air shows great improvement comparable to both unannealed and annealed ones in Ar. The enhancement mechanisms for both heterojunction and annealing are explored for fundamental insights, which reveal that the surface oxide layer can significantly increase the PEC stability of Ti:Fe_2O_3/CdSe photoanode. X-ray photoelectron spectra and transmission electron microscope results further confirms the surface oxidation on CdSe layer after annealing in air.

Introduction

Photoelectrochemical water splitting is very promising to produce renewable energy [1–5]. Great endeavour has been paid to study Fe_2O_3 based photoanodes. Fe_2O_3 has some prominent advantages including suitable valence band, excellent chemical stability, non-toxicity and abundant reserve [6–9]; however, it still suffers from poor charge separation efficiency and sluggish kinetics [10–12]. Formation of heterojunction is an effective strategy to improve the charge separation efficiency and expand the response range of solar spectrums [13–17]. Some Fe_2O_3 based heterojunctions have been reported to improve the PEC performance, such as Pt:Fe_2O_3/Co-Pi, Ti:Fe_2O_3/Cu_2O, Ti:Fe_2O_3/$Ni(OH)_2$, Ti:Fe_2O_3/FeOOH and so on [10,18–20]. CdSe is an n-type semiconductor with a narrow band gap of 1.74 eV, which has a widely spectral

* *Corresponding author*. Institute for Clean Energy & Advanced Materials, Faculty of Materials and Energy, Southwest University, Chongqing 400715, PR China.
E-mail address: ecmli@swu.edu.cn (C.M. Li).
[1] These authors contributed equally to this work.

https://doi.org/10.1016/j.ijhydene.2018.05.142

Please cite this article in press as: Xiong J, et al., Significantly improve photoelectrochemical performance of Ti:Fe_2O_3 with CdSe modification and surface oxidation, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.142

absorption ability from ultraviolet light to 712.6 nm red light [21,22]. Numerous works have demonstrated that the heterojunction based on CdSe and other semiconductors such as ZnO and TiO_2 could greatly improve their PEC performance, in particular the photocurrent density [23–26]. Nevertheless, CdSe-modified Ti:Fe_2O_3/CdSe heterojunction has not been investigated yet.

Normally, CdSe has a poor stability under light illumination in electrolyte or in air. The surface oxidation and the decomposition of CdSe quantum dots have been observed [27]. Annealing is a usually used procedure to improve the crystalline, remove the surface contaminants and eventually enhance the performance of a PEC cell [28–31]. Tracey et al. reported that Fe_2O_3 were annealed to form nanorods and nanocorals in the oxygen-rich and oxygen-poor atmospheres, respectively [32]. Bianca et al. explored the effects of annealing on Fe_2O_3 in air and argon atmospheres, which that the oxygen-poor atmosphere can enhance the PEC performance [33]. In addition, Chi et al. tested the effect of annealing temperature on CdSe/TiO_2, and revealed that CdSe/TiO_2 had the best performance at 300 °C [34]. Ai et al. reported the performances of CdSe/TiO_2 annealed in different temperatures and in different atmospheres. However, the mechanism for annealing in different atmospheres leading to different performances have not been investigated deeply [35]. As above, no one has carefully studied the role of Ti:Fe_2O_3/CdSe heterojunction in PEC cell and the effect of annealing on this system. Although there have been intensive studies on the formation of heterojunctions based on ZnO, TiO_2 with CdSe, Fe_2O_3 has the stronger chemical stability and a narrower band gap than that of ZnO and TiO_2, which could be a valuable candidate for solar energy applications. It is very interesting to investigate the PEC behaviours of Ti:Fe_2O_3/CdSe heterojunction and its annealing effect for both scientific significance and practical applications.

In this work, CdSe is used to modify Ti:Fe_2O_3 photoanode forming Ti:Fe_2O_3/CdSe heterojunction. Combining with an air annealing treatment, Ti:Fe_2O_3/CdSe exhibits a 6.5 times higher photocurrent than the pristine Ti:Fe_2O_3 to achieve 3.25 mA cm^{-2} at 1.2 V vs. RHE. Its photoelectrochemical stability after annealling treatment in air shows significant improvement comparable to both unannealed and annealed ones in Ar. The improvement mechanism is clearly revealed by X-ray photoelectron spectra and transmission electron microscope. This work provides new scientific insights to improve the photostability of CdSe like semiconductors.

Experimental section

Ti doped hematite photoanode preparation

Fluorine-doped tin oxide (FTO) glass was sequentially cleaned in acetone, ethanol and distilled water for 20 min, respectively. α-Fe_2O_3 film was prepared according to the method reported in literature [36]. First, 0.15 M $FeCl_3 \cdot 6H_2O$ were dissolved in water. FTO was vertically placed in above solution, and maintained at 100 °C for 5 h to form orange film. Then, 0.06 ml solution contained ethanol and isopropyl titanate (v/v, 50/1) was dropped onto the above orange film. After drying, the film was initially annealed in air at 550 °C for 2 h, then at 800 °C for 20 min and followed by 5 min annealing time at 550 °C. After annealing, the orange film changed into deep red film due to the transition from FeOOH to Ti:Fe_2O_3.

CdSe sensitization

The solution consisting of 0.02 M $Cd(Ac)_2$, 0.02 M Na_2SeO_3, and 0.04 M EDTA−2Na was used to electrodeposit CdSe onto the Ti:Fe_2O_3 film [37]. The FTO substrate covered with Ti:Fe_2O_3, a Ag/AgCl electrode and a platinum sheet served as the working electrode, the reference electrode and the counter electrode, respectively. Then Ti:Fe_2O_3/CdSe can be obtained by electrodepositing at the current of −1 mA cm^{-2}. Then, the Ti:Fe_2O_3/CdSe was annealed at 350 °C in air for 1 h.

Material characterizations

X-ray diffraction (XRD) analysis was conducted by a Shimadzu XRD-7000 diffractometer. The surface morphology of the samples were examined by JEOL JSM-7800F field emission scanning electron microscope (FESEM). The ultraviolet-visible (UV-Vis) absorption spectra of the samples were obtained by a Shimadzu UV−vis recording spectrophotometer (UV-2550) using $BaSO_4$ as the reference. X-ray photoelectron spectroscopy (XPS) were collected on an ESCALAB 250Xi and calibrated with C1 s at 284.4 eV.

PEC performance measurements

Photoelectrochemical performances were measured with an electrochemical analyzer (Zahner Zennium) in a three-electrode configuration using the prepared sample as working electrode, Ag/AgCl as a reference electrode (CHI-111), Pt electrode as a counter electrode. The measured potential vs the Ag/AgCl (sat. KCl) reference electrode was converted to the reversible hydrogen electrode (RHE) scale following the Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.0591 \times pH + 0.1976$ (at 25 °C). The electrolyte was 0.25 M Na_2S and 0.35 M Na_2SO_3 with a pH level of 13.6.

A 300W xenon lamp (CEL-HXF300E/CEL-HXUV300E, CEAULIGHT) provided AM 1.5 G simulated sunlight, and the light intensity was adjusted to 100 mW cm^{-2}. The effective illumination area is 1.0 cm^2, which is well-confined by surface insulating adhesive tape. All the photoelectrochemical measurements were done from the front side of FTO glass. The linear sweep voltammogram (LSV) curves were recorded at a scan rate of 20 mV/s. Photoelectrochemical impedance spectroscopy (PEIS) was obtained at 1.2 V_{RHE} and with an AC amplitude of 10 mV and frequency range between 100 kHz and 0.1 Hz.

Results and discussion

Effects of CdSe sensitization

The effects of CdSe sensitization on Ti:Fe_2O_3 were studied firstly. As shown in Fig. 1a, the morphology of Ti:Fe_2O_3 prepared by the solution-based method with the post annealling

Please cite this article in press as: Xiong J, et al., Significantly improve photoelectrochemical performance of Ti:Fe_2O_3 with CdSe modification and surface oxidation, International Journal of Hydrogen Energy (2018), https://doi.org/10.1016/j.ijhydene.2018.05.142