INTERNATIONAL JOURNAL OF HYDROGEN ENERGY 42 (2017) 20879–20887

Available online at www.sciencedirect.com

ScienceDirect

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

Efficient photoelectrochemical water splitting and impedance analysis of WO_{3-x} nanoflake electrodes

S.Q. Yu, Y.H. Ling*, J. Zhang, F. Qin, Z.J. Zhang

Lab of Advanced Materials, School of Materials Sciences and Engineering, Tsinghua University, Beijing 100084, China

ARTICLE INFO

Article history:
Received 1 November 2016
Received in revised form
3 January 2017
Accepted 29 January 2017
Available online 17 February 2017

Keywords:
Tungsten trioxide
Nanoflake
Photoelectrochemical
Water splitting

ABSTRACT

Solar-powered water splitting with photoelectrochemical (PEC) devices is considered to be a promising method to simultaneously harvest and store solar energy at a large scale. Nanostructured semiconductors offer potential advantages in PEC application due to their large surface area and size-dependent properties, such as increased absorption coefficient, increased band-gap energy and reduced carrier-scattering rate. In this contribution, self-doped tungsten trioxide (WO_{3-x}) nanoflake arrays were synthesized via a new route which involves the dealloying of Fe–W amorphous alloy, thermal treatment in air and properly cathodic polarization. The effects of different cathodic polarization current leading to different x value in WO_{3-x} on the morphology, phase, and photoelectrochemical performance of the resultant samples were investigated. It was found that WO_{3-x} with the appropriate x value presents a dramatic photoelectrochemical current density of 8.7 mA cm^{-2} in the presence of methanol as a hole scavenger, five folds larger than that of pristine WO_3 nanoflakes. UV–vis reflection spectra suggest that the light absorption spectrum range of WO_{3-x} extends from UV to visible light region. Electrochemical impedance spectroscopy disclosed that the unique nanoflake architecture and the surface defects offer improved light harvesting as well as efficient charge transportation.

Introduction

Nowadays, the research for efficient and sustainable energy is motivated because of strict environmental regulations and rising global energy demand [1]. Hydrogen has great potential because it is the most abundant element, has a high energy density and can be transported directly [2]. Extracting hydrogen from water by solar-driven photoelectrochemical water splitting [3,4]has been of considerable interest since TiO_2 was discovered as photoanode in this process by Fujishama and Honda in 1972 [5]. Whether this process will be successful depends on the development of semiconductor materials which demands to satisfy band-edge positions, be stable and efficient in solar absorption [6,7]. Transition metal oxides are the most available photoanode materials [8,9].

Considering all the inherent properties of these metal oxides, WO_3 is one of the most promising photo anodes with 2.6 eV band gap, appropriate band gap position, photo corrosion resistance ability in aqueous solution and chemical stability in acid [10,11]. However, its photoelectron conversion efficiency reported is still far away from what has been estimated theoretically at 6.3% due to light absorption and recombination of electron–hole pair [12–14]. In order to prevent the electron–hole pair recombination, organic

* *Corresponding author*. Fax: +861062772507.
E-mail address: yhling@mail.tsinghua.edu.cn (Y.H. Ling).
http://dx.doi.org/10.1016/j.ijhydene.2017.01.177

compound such as methanol which requires a lower energy is mixed with water in electrolyte to accelerate production of hydrogen [15]. Besides, morphology modification and various doping methods in WO_3 are used to improve charge transport properties and light absorption efficiency, so that photoelectrochemical performance can be enhanced [16–18].

Two-dimensional WO_3 nanoflake arrays exhibit enhanced photoelectrochemical water splitting ability, as the optical thickness of the photoelectrodes is increased by light scattering at the nanostructured interfaces [19,20]. And electron–hole pair separation is more efficient when the diffusion pathway of photogenerated holes is comparable to the dimension of the nanoflake [21]. For instance, tungsten trioxide/bismuth vanadate heterojunction with helical nanostructures has been fabricated for PEC solar water splitting and a photocurrent density of 5.35 mA cm^{-2} was achieved by Shi et al. [21]. Various chemical and physical techniques have been used to synthesize different forms of WO_3 nanostructures, including hydrothermal method [22], anodization [23], sol–gel method [24], chemical vapor deposition [25] and so on. However, precisely controlled conditions and surface morphology is still needed in the fabrication of WO_3-based photo anode.

Despite the enhanced electron–hole pair separation, two-dimensional WO_3 nanoflake array generally still has limited light absorption spectrum range [26]. To solve this problem, one feasible strategy is doping pure WO_3 with various elements to narrow its band gap [27,28]. For example, Fe-doping WO_3 with nanostructure has been synthesized by Zhang, who found that extra band states formed by doping promoted its PEC water splitting performance by 30% [27]. Unfortunately, severe thermal instability and less efficient electron–hole pair separation resulted from these doped elements, crippling photoelectrochemical water splitting ability of WO_3 photo anode [29]. Recently, introducing W ions with lower valence or O vacancy to WO_3 nanoflake arrays to form local states at WO_3 conduction band bottom for water splitting has attracted much attention [30]. Compared with conventional impurity species doping, O vacancies in WO_3 can not only expand light absorption range and increase electrical conductivity, but also they can make electron–hole pair separating effectively while promoting thermal stability at the same time [31]. Wang et al. succeeded to introduce oxygen vacancies into WO_3 through hydrogen atmosphere at elevated temperature, enhancing its photoactivity for water oxidation [11]. Zhang et al. synthesized metallic/semiconducting HWO_3/WO_3 nano heterostructure for near-infrared photocatalysis, in which H_xWO_3 is proved to favor electrons transfer [32]. Liu et al. reported situ homospecies WO_3 film by electrochemical doping to improve the PEC water splitting performance [33].

Taking advantage of the structure of nanoflake arrays and O vacancy in WO_{3-x}, the efficiency of PEC water splitting can be significantly improved. In this paper, we synthesized novel self-doped tungsten trioxide (WO_{3-x}) nanoflake arrays via a new and extremely facile route which involves electrodeposition and dealloying of Fe–W amorphous alloy, thermal treatment in air and properly cathodic polarization. Morphology, crystal structure, chemical state and the as-fabricated WO_{3-x} were investigated. PEC performance was analyzed in methanol/water solution. These self-doped nanoflake arrays with appropriate x value exhibit a wider light absorption range and more efficient PEC performance than pristine WO_3. In addition, a mechanism of this enhanced water splitting property was disclosed by electrochemical impedance spectroscopy (EIS).

Experimental details

Material preparation

Self-doped WO_{3-x} nanoflake arrays were firstly prepared by a two-step dealloying process and then reduced in HNO_3 aqueous solution with a bias potential.

Fe–W amorphous alloy cathodically electro-deposited on commercial stainless steel was the first step. Stainless steel slices (10 × 20 mm) were mechanically polished with SiC paper of grit sizes ranging from #800 to #2000 and then ultrasonically washed in acetone, water and alcohol. Two-electrode cell electro-deposited equipment included: the above stainless steel as cathode, graphite paper as anode and aqueous solution containing 10.5070 g $C_6H_8O_7 \cdot H_2O$, 16.4930 g $Na_2WO_4 \cdot 2H_2O$, 1.3900 g $FeSO_4 \cdot 7H_2O$ and 100 mL H_2O as electrolyte. Amorphous alloy was deposited at a 0.03 A cm^{-2} current density for 80 s in a 60 °C water bath environment.

Dealloying of the Fe–W amorphous alloys was the second step. The as-deposited amorphous alloy was immersed in 3.5 wt% HNO_3 aqueous solution for 20 h in room temperature. This dealloying process was accompanied by a conspicuous color change from transparent to faint yellow. Subsequently WO_3 nanoflake arrays were annealed at 500 °C for 3 h in a furnace chamber. Finally, the as-prepared nanoflake arrays were cathodic polarized in 100 mL aqueous solution with 0.5 mL 68 wt% HNO_3. To investigate the effect of reduction degree of WO_3 on PEC activity, a series of WO_{3-x} with different x value were prepared at different reduction potential for 30 min under identical conditions.

Material characterization

The as synthesized film were characterized by FE-SEM(JEOL JSM-7001F) at 20 kV, XRD(D/max-2500, Cu Kα radiation), Raman(Renishaw RM2000, 100–1000 nm), TEM(JEOL JEM 2011) and X-ray photoelectron spectroscopy(XPS, ESCALAB 250Xi, Thermo Fisher SCIENTIFIC, US). The optical properties of the film were examined by UV–vis spectrometer (PE, L950) and photoluminescence (Edinburgh Instruments, FLS920).

Photoelectrochemical measurements

PEC measurements were carried out in 0.5 M H_2SO_4 with volume ratio of H_2O and methanol to be 9:1. A standard three-electrode cell of as-prepared film as work electrode, platinum foil acted as counter electrode, and a saturated calomel electrode acted as reference electrode was involved. Zahner IM6e universal electrochemical interface analyzer was used to record photoelectrochemical signals and a 100 mW cm^{-2} xenon arc lamp was served as light source. All these PEC measurements were implemented in ambient conditions.