Electrochimica Acta 274 (2018) 217–223

Contents lists available at ScienceDirect

Electrochimica Acta

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

Oxygen vacancy engineering of WO_3 toward largely enhanced photoelectrochemical water splitting

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ARTICLE INFO

Article history:
Received 11 January 2018
Received in revised form
29 March 2018
Accepted 16 April 2018
Available online 17 April 2018

Keywords:
Photoelectrochemical water splitting
Oxygen vacancy
WO_3 photoanode

ABSTRACT

Photoelectrochemical (PEC) water splitting plays a crucial role in clean and renewable energy production, in which solar-to-chemical energy conversion efficiency is definitively dependent on the charge carrier generation and transfer ability. Here we report a facile and effective method to largely enhance the transfer ability of charge carriers *via* fabrication of an oxygen vacancy-rich WO_x modulated WO_3 photoanode (WO_3-OV). Experimental studies show that the oxygen vacancies significantly increase the charge carrier density of WO_3-OV (~6.89 times larger than that of pristine WO_3). Moreover, density functional theory calculations reveal that a WO_3/WO_x heterojunction is formed due to the energy difference between WO_3 and oxygen vacancy-rich layer, which improves the build-in electronic field and reduces the charge recombination. As a result, the WO_3-OV photoanode gives largely improved charge separation efficiency (67.2%) and a high photocurrent density of 1.35 mA cm^{-2} at 1.23 V *vs.* RHE, among the highest level in WO_3-based materials. It is expected that the surface modulation by oxygen vacancy can be extended to other semiconductor systems for advanced performance in the fields of energy conversion and storage.

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1. Introduction

Photoelectrochemical (PEC) water splitting has been recognized as one of the promising technologies for the production of hydrogen fuel from solar energy to address the increasing global demand for clean energy [1–3]. To promote the PEC process, an efficient photoanode which generates electron and hole pairs for the surface redox reactions is highly required. Although various photoanodes (e.g., TiO_2 [4,5], Fe_2O_3 [6,7], and $BiVO_4$ [8,9]) have been extensively studied for water splitting, the solar-to-chemical energy conversion efficiency is still limited by photo-generation and transfer abilities of charge carriers. For a given photoanode, the photo-generated carriers only can be utilized on the semiconductor/electrolyte (sem/ele) interface for the subsequent redox reactions after migrating through bulk region and depletion layer. The existence of defects and destruction of crystal periodic potential field provide abundant recombination centers, which restricts the utilization of charge carriers [10,11]. Therefore, the effective reduction of charge recombination and simultaneous enhancing charge utilization efficiency at (sem/ele) interface is significant for high-performance photoanodes.

Tungsten oxide (WO_x, $0 < x \leq 3$), a nontoxic and photo-stable *n*-type semiconductor, has shown promising PEC performance with a high theoretical utilization efficiency of solar energy, but still suffers from a facile recombination of electron-hole pairs [12–16]. It is reported that oxygen vacancies as electron donors can enhance the formation of depletion layer in sem/ele junction, which thereby facilitates the charge carriers separation [17–19]. However, the presence of oxygen vacancies normally introduces new recombination sites of charge carriers (twisty lattice or surface state), which is contradictory to the improvement of PEC performance. To address this issue, the introduction of oxygen vacancies with less charge recombination center is highly desirable to enhance the charge separation in WO_3 materials.

Herein, we report a facile and effective method to enhance the transfer ability of charge carriers by the fabrication of an oxygen vacancy-rich WO_x layer modified WO_3 photoanode (denoted as WO_3-OV). In comparison with the pristine WO_3, the obtained WO_3-OV photoanode exhibits a largely improved charge separation efficiency of 67.2% (2.67 times higher than WO_3) and a photocurrent density of 1.35 mA cm^{-2} at 1.23 V *vs.* RHE, which is among the highest level in WO_3-based photoanode. The Raman and electron

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https://doi.org/10.1016/j.electacta.2018.04.109
0013-4686/© 2018 Published by Elsevier Ltd.

paramagnetic resonance (EPR) results confirm the generation of oxygen vacancies in WO_3-OV; density functional theory (DFT) calculations reveal that the suitable bandgap of WO_3-OV promotes the formation of self-build electric filed in depletion layer. This facilitates the hole transfer from WO_3-OV bulk region to the sem/ele interface, giving rise to the significantly enhanced PEC water splitting performance.

2. Experimental

2.1. Preparation of WO_3 and WO_3-OV photoanodes

The WO_3 arrays were prepared on FTO substrate using a modified hydrothermal method [20,21]. In a typical synthesis, 0.825 g of $Na_2WO_4 \cdot 2H_2O$ and 0.425 g of $NaNO_3$ were dissolved in 25 mL of deionized water, followed by the addition of HNO_3 (2 M) to adjust the pH value to be ~1.5. The as-prepared solution was then transferred into a Teflon-lined stainless steel autoclave. One piece of cleaned FTO glass substrate (2 cm × 5 cm) was placed at an angle against the wall of reactor with the conducting side facing down in advance. Hydrothermal treatment was carried out at 100 °C for 6 h. The product was collected and washed with deionized water (defined as $WO_3 \cdot 0.33H_2O$ arrays). The WO_3 arrays were obtained by annealing at 550 °C for 2 h in air.

The WO_3-OV arrays were obtained by spin-coating of a H_2WO_4 suspension (~0.2 mg mL^{-1}) several times onto the prepared $WO_3 \cdot 0.33H_2O$ arrays, followed by annealing at 550 °C for 2 h in air. In this annealing process, H_2WO_4 transformed to tungsten oxide (WO_x) with more oxygen vacancy. In addition, WO_x photoanode was prepared by spin-coating of a H_2WO_4 suspension several times onto the FTO substrate, followed by the same annealing process.

2.2. Preparation of CoPi modified WO_3 and WO_3-OV photoanodes

Photo-assisted electrosynthesis of CoPi was performed by a modified procedure [22]. The CoPi was deposited in a three-electrode configuration by using WO_3 or WO_3-OV as working electrode, Pt wire as counter electrode, and saturated calomel electrode (SCE) as reference electrode in a solution of 0.5 mM cobalt nitrate in 0.1 M potassium phosphate buffer at pH 7 with illumination. The potentiostatic deposition was carried out at a potential of 0.4 V *vs.* SCE with light illumination at a power density of 100 mW cm^{-2} by a 150 W Xe lamp. The amount of CoPi deposited can be controlled by the deposition time (300s).

2.3. Characterizations

The morphology was investigated using a scanning electron microscopy (SEM; Zeiss SUPRA 55) with an accelerating voltage of 20 kV. High resolution transmission electron microscopy (HRTEM) images were recorded using a Hitachi H-800 TEM with an accelerating voltage of 200 kV. X-ray diffraction (XRD) patterns were collected on a Rigaku XRD-6000 diffractometer using Cu Kα radiation with a scan step of 10° min^{-1}. Raman spectra were collected on a LabRAM ARAMIS Raman system using a 532 nm laser as the excitation source. Solid UV–vis diffuse reflection spectra were collected on a Shimadzu U-3000 spectrophotometer. Fluorescence spectra were recorded on a RF-5301PC fluorospectrophotometer with an excitation wavelength of 300 nm. EPR data were measured at room temperature on a Bruker E500 Electron Paramagnetic Resonance Spectrometer.

2.4. Photoelectrochemical measurements

PEC water splitting performances were operated on an electrochemical workstation (CHI 660e, CH Instruments Inc., Shanghai) at room temperature in a neutral medium of Na_2SO_4 (0.5 M) aqueous solution with a three-electrode optical cell. Illumination source was a 300 W Xe lamp with a power density of 100 mW cm^{-2}. The working, counter (a Pt wire), and reference (a saturated calomel electrode (SCE)) electrode are installed in a quartz cell. The photocurrent was measured by cyclic voltammetry (CV) or linear sweep voltammetry (LSV) at a scan rate of 10 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was carried out by applying an AC voltage at 1.03 V *vs.* RHE with frequency ranging from 100 kHz to 0.1 Hz under illumination. Mott-Schottky plots were evaluated at DC potential range from 0 V to 1.1 V at a frequency of 1 kHz.

The E_{RHE} was calculated by:

$$E_{RHE} = E_{SCE} + E^{\theta}_{SCE} + 0.059 \times \text{pH}$$

where E_{SCE} is the applied bias *vs.* SCE and $E^{\Theta}{}_{SCE}$ is the standard electrode potential of SCE (0.2438 V at 25 °C).

The photoconversion efficiency (η) was calculated using the following equation:

$$\eta = J \times (1.23 - E_{RHE}) \Big/ P_{light}$$

where E_{RHE} is the applied bias *vs.* reversible hydrogen electrode (RHE); J is the photocurrent density at the measured bias, and P_{light} is the irradiance intensity of 100 mW cm^{-2}.

The incident photon to current efficiency (IPCE) was evaluated at 1.23 V *vs.* RHE under monochromatic light irradiation by using a system comprising a monochromator (CEAULIGHT IS151), a 300 W Xe lamp and a calibrated silicon photodetector. IPCE was calculated by the equation:

$$\text{IPCE} = (1240 \times J_{mono}) / (P_{mono} \times \lambda)$$

where J_{mono} is the measured photocurrent density at a specific wavelength; P_{mono} is the measured irradiance at a specific wavelength, and λ is the wavelength of incident light.

3. Results and discussion

The preparation of WO_3 and WO_3-OV arrays on fluorine-doped tin oxide (FTO) is illustrated in Fig. 1a (see details in the experimental section). The $WO_3 \cdot 0.33H_2O$ precursor were firstly grown on a FTO substrate *via* a modified hydrothermal method, which was then transformed to WO_3 arrays by an annealing process with the sample color change from white to green. WO_3-OV arrays were prepared by spin-coating of tungstic acid (H_2WO_4) solution onto $WO_3 \cdot 0.33H_2O$ precursor followed by the same annealing process. As a reference sample, powdered sample of tungsten oxide (denoted as WO_x) was prepared by directly annealing H_2WO_4 solution on FTO substrate. As shown in the XRD patterns (Fig. 1b), three sharp reflections located at 14.1°, 18.1° and 28.3° are observed for the $WO_3 \cdot 0.33H_2O$ precursor, corresponding to the (020), (111) and (220) reflection of tungsten hydrate (JCPDS No. 35-0270), respectively. Both the WO_3 and WO_3-OV samples show the (002), (020), (200) reflection of a typical γ-WO_3 phase at 23.1°, 23.6°, 24.4°. In case of WO_x, a slight high angle shift of (002), (020), (200) reflection is observed compared with WO_3 (Fig. S1). The self-doping of oxygen vacancies is facile to form on the distorted structures in the dehydration process of tungsten oxide hydrate precursor. The titling angles and rotation directions of the basic unit WO_6 octahedra in tungsten oxides determines the composition of WO_x, which largely inherit the precursor crystal structure [23]. So two different stoichiometry tungsten oxides (WO_3 and WO_x) are formed

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