Journal of Alloys and Compounds 691 (2017) 750–754

Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Hydropowered photoelectrochemical water splitting solar cell for hydrogen production

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ARTICLE INFO

Article history:
Received 11 April 2016
Received in revised form
27 May 2016
Accepted 27 August 2016
Available online 30 August 2016

Keywords:
Atomic layer deposition
Photoanode
Hydroelectric generator
Bias potential
PEC performance

ABSTRACT

Photoelectrochemical (PEC) water splitting has been considered to be a promising route for sustainable hydrogen production from the solar energy. However, owing to the suitable potential required for such process, the external bias is usually indispensable on the PEC cell, which hinders its wide application. In this paper, we integrated the PEC cell with hydroelectric generator for water splitting, where the bias potential of the PEC was supplied from its water environment. The ZnO and TiO_2 films were prepared on conductive FTO substrates for photoanodes by magnetron sputtering and atomic layer deposition, respectively, while structures and morphologies of the films were characterized by XRD and AFM. A three-electrode electrochemical cell configuration was performed to measure the PEC performance. The results demonstrate that PEC performance can be effectively facilitated when the PEC cell was connected with the hydroelectric generator, which suggests a promising route toward full green design for hydrogen production.

1. Introduction

Nowadays, energy supply has become the extremely urgent issue for all nations. Owing to the significant limitation of fossil fuel reserves as well as the more and more serious pollution and greenhouse gases emission problem coming along with the fossil fuel consumption, producing energy from renewable source holds great promises to solve the energy crisis and tackle the global warming issue [1–4]. Led by the pioneering discovery of the photocatalytic water splitting phenomenon on a TiO_2 electrode in early 1970s [5], extensive efforts have been made on developing highly efficient PEC cells [6–13]. Many semiconductors such as ZnO, CdS, CuO, TiO_2 and WO_3 have been tested in PEC cell devices. Among them, ZnO and TiO_2 are the most extensively studied materials due to their chemical stability, simple fabrication process, low cost, and nontoxicity [14,15]. So far, much related research is focused on enhancement of visible light utilization to improve the photocurrent of ZnO and TiO_2 based PEC cells. Zhigang Zang et al fabricated ZnO/Cu_2O solar cells with RF power of 0 W and the device showed a good rectifying behavior with an efficiency of 0.02% and a fill factor of 24% [16]. Xudong Wang et al reported a largely enhanced performance of PEC photoanodes by ferroelectric polarization-endowed band engineering on the basis of TiO_2/$BaTiO_3$ core/shell nanowires [17].

Thermodynamically, the minimum energy required for splitting H_2O into H_2 and O_2 is 1.23 eV. In fact, the potential in need is usually larger than 1.23 eV [18–20]. Therefore, an external bias potential is needed to overcome the kinetic barrier, which may consume electrical energy and lower the net energy conversion efficiency of the PEC cell. Meanwhile, conventional electrolysis of water for hydrogen production at the expense of electrical energy consumption is not worthy exploiting from the point of energy utilization [21]. Using wind energy, hydropower and other green renewable energy to achieve the hydrogen production is considered to be the best way of sustainable development in the future [22]. However, rare related paper was reported on this topic. In this work, we for the first time demonstrate the development of a self-biased voltage activated PEC water splitting of ZnO and TiO_2 photoelectrodes by combining the hydropower energy with PEC water splitting apparatus. Therefore, the paper provides a more feasible solution of full green PEC cell and shows promising applications in the future, which makes full use of the clean energy and decreases

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http://dx.doi.org/10.1016/j.jallcom.2016.08.290
0925-8388/

the energy consumption.

2. Experimental details

ZnO thin films were deposited on conductive FTO substrates at room temperature by magnetron sputtering using a metallic zinc target (99.99%). During the sputtering, the working pressure was kept at 0.25 Pa and the Ar/O_2 gas flow ratio was 3:1. The sputtering time was 15 min and the film thickness was about 100 nm TiO_2 thins films were deposited on FTO substrates by atomic layer deposition (ALD) method. The substrate temperature was 300 °C. The reactive sources were diethylzinc and H_2O with pulse time of 0.5 s and 0.5 s, respectively. Carrier gas was N_2 and the purging time was 60 s TiO_2 film with 600 ALD cycles has film thickness about 60 nm.

The crystal structure and surface morphology of ZnO and TiO_2 thin films were characterized by X-ray diffractometer (XRD, Tongda TD3000) and atomic force microscopy (AFM, Agilent technologies, Model N9451A), respectively. The prepared samples were then covered by epoxy, leaving an average exposed active area of ~1.4 mm^2 as the photoanodes. PEC characterizations were performed in 0.5 M Na_2SO_4 electrolyte using a three electrode electrochemical cell configuration. A saturated calomel electrode (SCE) was used as the reference electrode and a Pt sheet was used as the counter electrode. All electrodes were connected to a potentiostat system (CHI660D). Light illumination was provided by a 300 W Xe arc lamp (PLS-SXE300, Perfect Light). The intensity at the PEC anode position was adjusted to be 100 mW cm^{-2} with an AM 1.5 G filter and a UV cutoff 420 filter that cuts light with wavelengths ≥420 nm were also utilized for PEC characterizations. Amperometric I-t photoresponse was evaluated at an applied potential of 0.5 V vs. SCE.

3. Results and discussion

Fig. 1 shows the XRD patterns of magnetron sputtering ZnO and ALD TiO_2 films prepared on FTO substrates. The ZnO film shows strong preferential growth along (002) direction in Fig. 1(a), which is consistent with our previous results. The XRD analysis of Fig. 1(b) shows that ALD TiO_2 film consists of anatase and rutile TiO_2 phases except some FTO substrate peaks, which confirms the polycrystallized structure of TiO_2 film.

Surface morphology of Fig. 2(a) shows smooth and homogeneous grain distribution with grain size about 100 nm. Preferential growth can be seen from Fig. 2(b), which was consistent with the XRD analysis. The root mean square (rms) roughness was evaluated to be 12.31 nm. While the 300 °C ALD deposited TiO_2 film has larger grain size about 150 nm with a dense surface morphology, which indicates good crystallinity of TiO_2 film. This is a result of stress release due to the higher mobility of the dislocations, producing more homogeneous films.

The PEC performances of the prepared samples and the unique self-biased voltage from hydroelectric generator design were investigated using our PEC system as schematically shown in Fig. 3(a), which mainly includes a home-made hydroelectric generator and PEC measurement equipment. The hydroelectric generator used electric motor (ASLONG RK-370CH/CA) and the rotation speed was about 120 r/min. A steady DC voltage of 0.5 V provided by the hydroelectric generator was connected to the ZnO photoelectrode. A three electrode configuration was used for PEC measurement with Pt sheet as the counter electrode and saturated calomel electrode (SCE) as the reference electrode. The water oxidation onset potential of ZnO photoanode was about 1.12 V vs SCE under darkness according to the linear sweep voltammograms of Fig. 3 (b) (Here we make the tangent at maximum slope of photocurrent and use the potential at the intersection point of the X axis [23,24]), while this value decreased to 0.93 V vs SCE when connected to the self-biased voltage generated from the hydroelectric generator. In addition, current density was obviously increased when connected with self-biased voltage. The photocurrent density showed a larger value due to the photocatalysis under AM 1.5 G illumination compared with that under darkness. It should be noted here that the photocurrent density can be further improved by using hydroelectric generators with higher voltage output such as accelerating the rotation speed of hydroelectric generator. Meanwhile the curve was wholly moved upward when connected with a self-bias voltage as shown in Fig. 3(c).

The chronoamperometric J-t curves of FTO/ZnO photoelectrodes attained at 0.5 V vs. SCE under darkness and AM1.5 G illumination were shown in Fig. 4(a) and (b), respectively. Under darkness condition, J-t curves of ZnO PEC cells showed very stable values during the 300 s measurement period. The current density with self-biased voltage was about 1.784 μA, which was nearly 10 times of the value without self-biased voltage. The photocurrent was caused by electrocatalysis reaction and no photocatalysis occurred under darkness condition, so the photocurrent density was greatly improved when self-biased voltage was applied to the FTO/ZnO photoelectrode.

For the ZnO PEC cells measured under Am 1.5 G illumination, the curve presents a slightly declining trend and the photocurrent density with self-biased voltage was only 1.5 times of the value without self-biased voltage due to the photocatalysis reaction. The

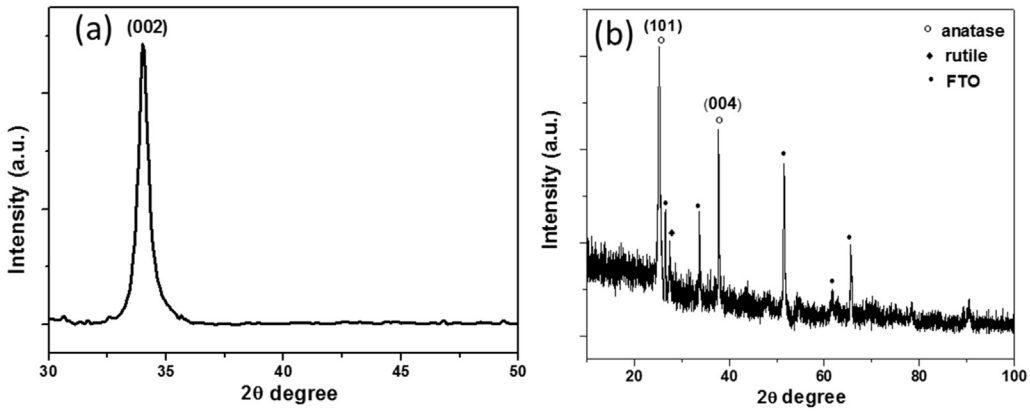

Fig. 1. XRD patterns of magnetron sputtering ZnO (a) and ALD TiO_2 films (b) prepared on FTO substrates.