Applied Surface Science 324 (2015) 414–418

Contents lists available at ScienceDirect

Applied Surface Science

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

NH_4-doped anodic WO_3 prepared through anodization and subsequent NH_4OH treatment for water splitting

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ARTICLE INFO

Article history:
Received 17 July 2014
Received in revised form
30 September 2014
Accepted 13 October 2014
Available online 22 October 2014

Keywords:
Tungsten oxide
Doping
Water splitting
Ammonium hydroxide
Anodic porous film

ABSTRACT

Tungsten trioxide (WO_3) prepared by anodization of a W foil was doped with NH_4 through NH_4OH treatment at 450 °C. Since aqueous NH_4OH was used during doping instead of NH_3 gas, the treatment step does not require complicated annealing facilities. Moreover, the state of doped N is a form of NH_3-W instead of W_2N, which lowers the bandgap but increases photocorrosion. We found that incorporation of NH_4 into WO_3 leads to reduction of the bandgap from 2.9 eV to 2.2 eV, regardless of the amount of NH_4OH treatment, lowering the onset potential and increasing the current density at fixed potential for oxygen evolution reaction under illumination. Scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy were employed to investigate the surface morphologies, crystallinities of tungsten oxides and existence of NH_4 doping, respectively. The bandgap energy was determined by UV–Vis spectroscopy to measure the transmittance and refraction. The water splitting performance of each sample was measured by electrochemical linear sweep voltammetry in a 3-electrode configuration under illumination.

1. Introduction

Tungsten trioxide (WO_3) has long been studied due to its versatile applications in gas sensors [1], electrochromic devices [2], and electrodes for photocatalysis [3]. Since WO_3 is a reliable and stable material that protects against photocorrosion during water splitting reactions [4–6], synthesis and characterization of nanostructured tungsten oxide as photoanode electrodes has been intensively investigated with the goal of readily reaching saturated photocurrent under external bias with the smallest overpotential possible [7].

The nanostructure of WO_3, which is typically used as an n-type semiconductor, has a relatively far longer minority carrier lifetime than hematite (α-Fe_2O_3), indicating that it is relatively stable in acidic media and has a less positive onset potential [8–11]. However, only a small portion of the solar spectrum is absorbed by WO_3 because of its large indirect band-gap energy (2.5–3.0 eV) [12–15].

Sol–gel [16], hydrothermal [17], solvothermal [18], anodization [13,14,19,20], sputtering [15,21], and chemical vapor deposition (CVD) [22] have been reported as methods for preparing well-controlled nanostructured WO_3.

Doping with foreign elements has also been attempted to customize the bandgap of WO_3 to produce efficient water splitting electrodes. High quantum efficiency has been reported to enable the poor spectral absorption to be overcome [23]. Different strategies for increasing quantum efficiency such as transition metal doping [24–26], noble metal deposition [27–29], dye sensitization [30], and organic material absorption [31] have been studied.

Although nitrogen doping is an effective method of reducing the bandgap of WO_3, the effects of N-doping on the photoelectrochemical (PEC) performance of WO_3 films have been controversial [14,15,22].

Nah et al. reported that nanoporous WO_3 could be prepared by simple anodization and subsequent annealing at 300 °C under NH_3 gas. As a result, N-doped WO_3 showing significant enhancement of photocurrent in the visible light region was prepared [13]. Cole et al. reported that WO_3 film with a doping of N was fabricated by RF sputtering. In their study, the optical bandgap of WO_3 was reduced to 2.0 eV; however, the photocurrent was reduced due to degradation of electron transport caused by the defective lattice. Formation of W_2N via conversion from WO_3 by NH_3 gas significantly reduced the bandgap from 2.9 eV to 2.2 eV, but increased instability of the photoelectrode due to photocorrosion and defects. In addition, electrons were easily recombined since grain size and

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http://dx.doi.org/10.1016/j.apsusc.2014.10.059
0169-4332/

crystallinity decreased in response to N-doping of defective sites [15]. It is possible that these opposing effects are responsible for the controversial results.

In this study, nanoporous WO_3 films prepared by anodization in non-fluoride based electrolytes were doped by a wet-based method using ammonium hydroxide (NH_4OH) instead of NH_3 gas; thus, complex gas facilities were not required for annealing. As a result of using NH_4OH, new phases $(NH_4)_{10}W_{12}O_{41}$ were generated, leading to the reduced bandgap. In addition, the PEC performance in 0.33 M H_3PO_4 was comparable to that of the existing NH_3 treatment.

2. Experimental

Prior to anodization, tungsten foils (Goodfellow, England, 99.95%, 0.33 mm) were cleaned with acetone, isopropanol and deionized (DI) water for 10 min in air at room temperature. The nanostructured WO_3 films were prepared in a 2-electrode configuration cell by applying constant potential at 50 V with a SourceMeter (Keithley 2400, US) at 95 °C for 20 h. During the process, 10 wt.% K_2HPO_4/glycerin anhydrous solution was used as the electrolyte, which was heated at 195 °C for 3 h to eliminate the moisture. After anodization, the fabricated WO_3 films were rinsed with isopropanol and DI water and then annealed for 1 h at 450 °C with different amounts (1, 2, and 3 g, corresponding to 0.029, 0.058, and 0.087 M, respectively) of NH_4OH solution for NH_4-doping.

Field emission scanning electron microscopy (FE-SEM, S4300, Hitachi, Japan) was employed to characterize the surface morphology and thickness. The crystal phase and chemical surface state were determined by X-ray diffraction (XRD, Rigaku D/max-RB, Japan) and X-ray photoelectron spectroscopy (XPS, K-Alpha, Thermo Scientific, USA) with an Al-K α X-ray source. The indirect bandgap energy was calculated from a Tauc plot determined using a UV/Vis/NIR spectrophotometer (LAMBDA 750, PerKin Elmer, USA).

A 3-electrode configuration cell composed of an anode (metal oxide), cathode (Pt-mesh) and reference electrode (Ag/AgCl 3 M KCl) was employed to measure the photoelectrochemical performance in potential ranges of 0–2 V at a scanning rate of 10 mV/s in 0.33 M H_3PO_4 electrolyte under AM 1.5G illumination.

3. Results and discussion

Fig. 1 shows the top of the FE-SEM images of NH_4-doped anodic nanoporous tungsten trioxides, which were fabricated by annealing of anodic WO_3 under different amounts of NH_4OH. The thickness of metal oxide has been determined based on the applied anodizing voltage and post annealing temperature [32]. In this study, the anodizing voltage (50 V) and post annealing temperature (450 °C) were fixed to investigate the effects of the amount of NH_4OH on NH_4-doping in the structure. The NH_4 doped WO_3 layers had a thickness higher than that of the pure WO_3 layer because of the additional oxidation step.

X-ray diffraction and X-ray photoelectron spectroscopy were employed to determine the nitrogen state in WO_3 films. Fig. 2 shows the XRD patterns of nanoporous WO_3 prepared by anodization and annealing at 450 °C with or without NH_4OH treatment. Monoclinic WO_3 with preferential crystalline orientations of (0 0 2), (0 2 0), and (2 0 0) planes was confirmed at 23.119, 23.586, and 24.380°, respectively (JCPDS 43-1035). The intensity of WO_3 peaks has been reported to decrease as annealing temperature increased above 450 °C with NH_3 gas [13,14]. As shown in Fig. 2, NH_4OH treatment of samples at 450 °C led to formation of stable crystalline WO_3 layers, prohibiting the formation of W_2N phases. Note that peaks of

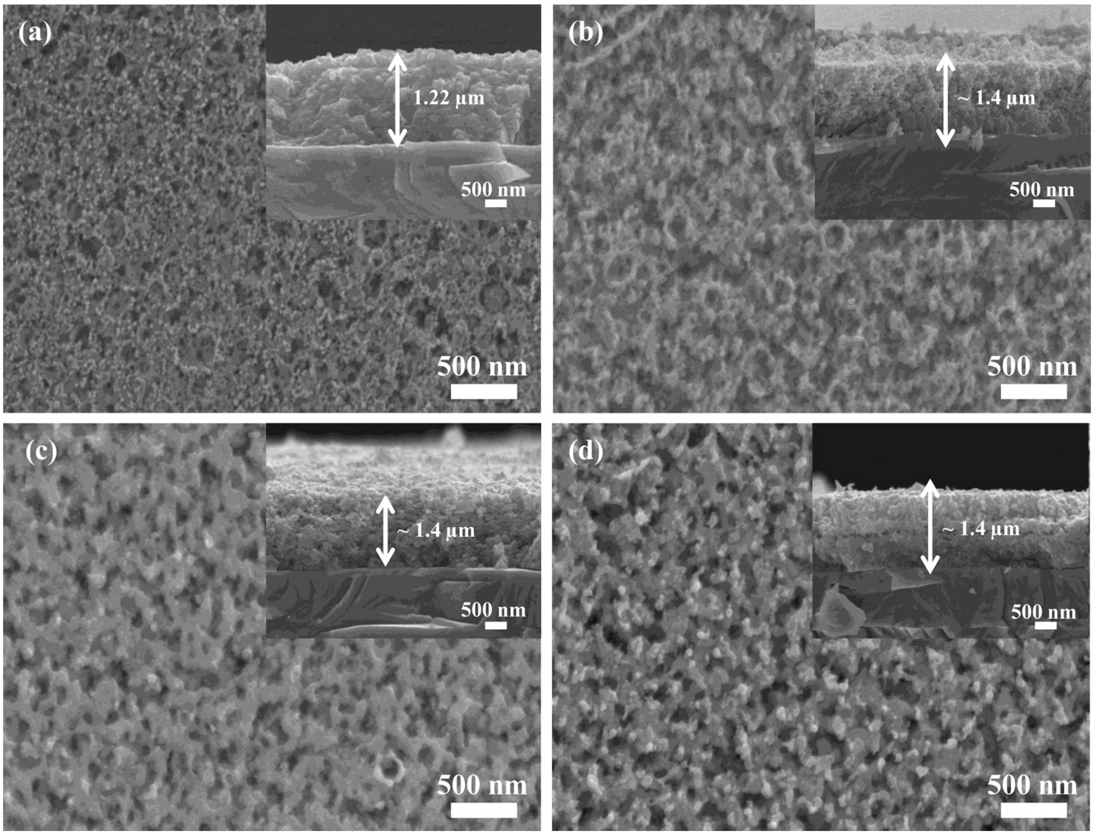

Fig. 1. FE-SEM images of the WO_3films prepared by NH_4-doping with (b) 0.029 M, (c) 0.058 M, and (d) 0.087 M NH_4OH, respectively. Fig. 1 (a) is the SEM image of the as-prepared anodic WO_3 film.