

Structural and photoelectrochemical investigation of boron-modified nanostructured tungsten trioxide films



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ABSTRACT

We report a modification of nanostructured WO₃ films by doping with boron. The films were obtained by a direct one-step sol–gel route involving tungstic acid/polyethylene glycol precursor. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that the incorporation of boron results in the retention of a substantial amount of water and/or hydroxyl groups in the WO₃ lattice and at the surface of nanoparticles occurring despite high temperature (550 °C) annealing of the films. Another consequence of boron doping is the largely increased roughness factor revealed by atomic force microscopy (AFM) imaging. Both kinds of films are highly porous and consist of partly sintered particles with sizes in the range of tens of nanometers. The photoelectrochemical (PEC) studies performed under simulated solar AM 1.5 illumination showed significantly enhanced water oxidation photocurrents for B-WO₃ photoanodes, by about 25% higher than those for the undoped WO₃ films of similar thickness. The low extent of recombination of photogenerated charges was confirmed by incident photon-to-current conversion efficiencies (IPCEs) reaching 70% in the region of visible wavelengths at 420 nm. The improved PEC properties were attributed to the increased surface hydroxylation of B-WO₃ nanoparticles favoring water photo-oxidation reaction and to the larger surface area of the film exposed to the electrolyte.

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1. Introduction

Photoelectrochemistry provides a means to store solar energy through converting water to oxygen and hydrogen [1]. Most of the recent research on H₂ production *via* photoelectrochemical (PEC) water splitting has focused on the use of n-type semiconductor metal oxide materials employed as photoanodes [1,2]. Following the first report by Fujishima and Honda of photo-oxidation of water on a rutile titanium dioxide (TiO₂) photoanode illuminated with ultraviolet (UV) light [3], initiated an extensive search of photoelectrode materials that are able to capture a substantial part of the visible spectrum. Early investigations involving a variety of inorganic semiconductors showed that the only materials able actually to split water whilst avoiding photocorrosion are metal oxides [4]. Besides investigations of TiO₂ doped with a variety of elements [2], the recent work centered on hematite (α -Fe₂O₃) [5] and tungsten trioxide (WO₃) [6] thin-film photoanodes with band gaps of 2.1 eV, respectively, 2.5 eV. Since any among these

materials having photoaction spectra covering visible wavelengths can perform unassisted water splitting, due to the position of the conduction band edges more positive than the H₂ evolution potential, continuing efforts are devoted to minimize the bias voltage required to perform visible light-driven photo-oxidation of water. Recently, unassisted solar production of H₂ has been demonstrated in a dual-absorber tandem device combining a semitransparent WO₃ photoanode and the latest version of the dye-sensitized solar cell (DSSC) providing a *ca* 1 V bias voltage to the photoelectrolyzer [7]. In such a tandem device, the WO₃ photoanode, deposited on the conductive glass substrate, absorbs the near-UV and blue-green portions of the solar spectrum and the DSS photovoltaic cell, placed behind the photoelectrolyzer, captures longer wavelengths transmitted by the WO₃ film.

Efforts toward implementation of the solar water splitting include also the search of the low-cost, effective in terms of the energy payback, preparation methods of photoelectrode materials. This is illustrated by a recent use of solution-based colloidal synthesis approach, instead of chemical vapour deposition method, which offers better PEC performance, to form thin layer α -Fe₂O₃ photoanodes [8].

In this paper, we report a modification with boron of nanostructured WO₃ films formed using simple, one-step, sol–gel

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method. The structure, surface composition and photoelectrochemical properties of WO_3 and B(III)- WO_3 films were studied. The B(III)-modified WO_3 photoanodes exhibit enhanced by about 25% water oxidation photocurrents which attain 2.15 mA/cm^2 at 1.23 V versus reversible hydrogen electrode (RHE), under standard solar conditions (AM 1.5). The incorporation of boron is found to increase roughness factor of the films and to induce retention of a significant amount of water and/or hydroxyl⁻ groups within the WO_3 structure, which are both proposed as contributing to the enhanced PEC performance. The increased hydroxylation, which is combined with excellent crystallinity of the B- WO_3 films, offers also attractive prospects for the application of this material in nanocomposite electrocatalysts for oxidation of alcohols [9].

2. Experimental

Nanostructured WO_3 films having thickness of approximately $1.2 \mu\text{m}$ were formed using a sol-gel method described in detail elsewhere [10,11]. Briefly, the employed precursor consisted of (poly)tungstic acid, freshly prepared by elution of a solution of Na_2WO_4 through the cation exchange column, and of an organic complexing agent (acting also as porogen), low molecular weight polyethylene glycol (PEG) 300. The WO_3/PEG ratio was 0.5 w/w. Boric acid (H_3BO_3) was a source of boron added to the precursor to obtain 10 at.%, respectively, 20 at.% B/W ratios. Fluorine-doped SnO_2 (FTO) conductive glass (Pilkington Glass, resistance 8–10 Ω/square) was used as a substrate. The FTO samples were first cleaned with acetone and then sonicated in deionized water for several hours. Some drops of the colloidal precursor were spread on the FTO substrate using doctor-blade technique, dried in air at 100°C and, subsequently, samples were annealed in flowing oxygen at 550°C for 30 min. The thickness of single WO_3 layers was 0.35–0.45 μm ; thicker films were formed by consecutive applications of the precursor, each followed by the annealing.

Raman spectra were acquired in the backscattering configuration with a Labram HR800 (Horiba Jobin Yvon) confocal microscope system equipped with a Peltier-cooled CCD detector (1024×256 pixel), using a 150 mW diode pumped, frequency doubled Nd:YAG laser (532 nm). The confocal pinhole size was set to 200 μm and the holographic grating with 600 grooves/mm was used. The instrument was calibrated using a 520 cm^{-1} Raman signal of a silicon wafer. All Raman spectra were obtained using a $100\times$ magnification Olympus objective. Deconvolution of the overlapping signals was conducted using the LabSpec5 software, assuming Gaussian shape of the Raman bands.

The X-ray photoelectron spectra (XPS) were taken on a PHI 5700 Physical Electronics spectrometer. Monochromatized X-ray Al ($K\alpha$) radiation of 1486 eV was used. The spectra were recorded with 23.50 eV pass energy, 0.100 eV step and 100 ms dwell time. The total energy resolution was about 0.35 eV. The measurements were performed in a vacuum of 10^{-10} Torr. Depth profiling was realized by sputtering with Ar^+ ions of 2 keV energy. The focused ion beam was scanned over the area $2.5 \text{ mm} \times 2.5 \text{ mm}$, whereas the analysis area had the diameter of 0.8 mm and was situated in the center of the created crater. The sputter rate was in the 1–2 nm/min rate. The XPS measurements were performed with the ion beam switched off.

The X-ray diffraction (XRD) patterns of deposited films and powder samples were measured on a Philips X'Pert diffractometer using $\text{CuK}\alpha 1$ radiation passed through a curved graphite monochromator. The patterns were recorded in the interval $15\text{--}140^\circ$, with the step of 0.02° . The crystal lattice, space group, cell parameters and site occupancies of the analyzed samples were evaluated from the corresponding XRD patterns, fitted and refined with a DBWS 9707 program.

A Veeco Nanoscope V atomic force microscope equipped with a (di) MultiMode V scanner was used for topography imaging.

Tapping mode AFM (TM AFM) was applied as less destructive toward the sample surface. Cantilevers with a spring constant of 42 N m^{-1} and resonance frequency range 311–380 kHz (manufacturer data), tuned prior to further measurement, were employed. The Nanoscope 7.30 software was used for topography visualization and cross-sectional profiling. The roughness parameter was calculated with aid of the NanoScope II software version 7.20. It is calculated as the difference between the image's three-dimensional surface area (this value is the sum of the area of all of the triangles formed by three adjacent data points) and two-dimensional projected surface area. The analysis was performed over the entire image.

A Teflon electrochemical cell with a quartz window, platinum foil counter electrode (separated from the photoanode by a Nafion membrane) and an $\text{Ag}/\text{AgCl}/\text{Cl}^-$ reference electrode was used for all photoelectrochemical studies. The photoanode (with the exposed surface area of 0.28 cm^2) was illuminated from the side of the WO_3 film/solution interface. Photocurrent action spectra (*i.e.*, incident photon-to-current conversion efficiencies plotted against excitation wavelength) were obtained by illuminating the sample with the light of a 500 W xenon lamp (Ushio UXL-502HSO), set in an Oriel model 66021 housing, passing through a Multispec 257 monochromator (Oriel) with a bandwidth of 4 nm. The absolute intensity of the incident light from the monochromator was measured with a model 730 A radiometer/photometer (Optronic Laboratories). The photocurrent–voltage characteristics were recorded by scanning the potential of the WO_3 photoanode at 10 mV s^{-1} under simulated AM 1.5 solar irradiation provided by an Oriel 150 W solar simulator fitted with a Schott 113 filter and a neutral density filter. The applied electrode potential versus $\text{Ag}/\text{AgCl}/\text{Cl}^-$ was converted to be reported versus the RHE at pH 2.

3. Results and discussion

The preparation of nanostructured WO_3 films relies on the sol-gel method involving a mixture of tungstic acid and polyethylene glycol (PEG). Deposition of the precursor on the FTO substrate followed by annealing in flowing oxygen at *ca* 550°C produces well crystallized WO_3 with monoclinic structure (*m*- WO_3). In fact, Raman spectra taken for both the boron (III)-modified and undoped films exhibit a series of features typical of *m*- WO_3 (Fig. 1). In particular, the strong bands lying around 715 and 805 cm^{-1} and weaker close to 270 and 325 cm^{-1} , corresponding, respectively, to the

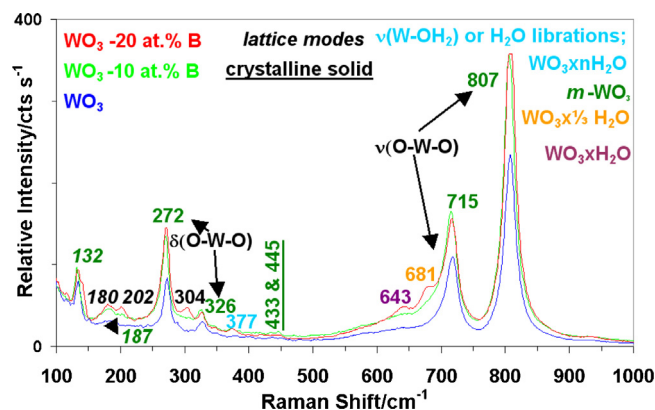


Fig. 1. Raman spectra, illustrating changes in the structure of tungsten trioxide induced by the addition of boron. The spectra, taken at $\lambda_{\text{exc}} = 532 \text{ nm}$, correspond to B-modified (at 10 and 20 at.%) and undoped *ca* $1.2 \mu\text{m}$ thick WO_3 films annealed at 550°C . The amount of boron added to the precursor and the assignments of different Raman modes are indicated in the legend. (For interpretation of the references to spectra in figure legend, the reader is referred to the web version of the article.)

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