

## Original article

# Synthesis of $\alpha$ -SnWO<sub>4</sub> thin-film electrodes by hydrothermal conversion from crystalline WO<sub>3</sub>



Kayla J. Pyper, Taylor C. Evans, Bart M. Bartlett\*

Department of Chemistry University of Michigan, Ann Arbor, MI 48109-1055, USA

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## ABSTRACT

Thin film electrodes of the orthorhombic form of tin tungstate ( $\alpha$ -SnWO<sub>4</sub>) were prepared using a hydrothermal method to convert thin films of WO<sub>3</sub> in aqueous SnCl<sub>2</sub>. The pH dependence of the growth mechanism was identified by scanning electron microscopy (SEM) and X-ray diffraction (XRD). The XRD patterns show complete conversion of WO<sub>3</sub>(s) to SnWO<sub>4</sub>(s) at pH 1, 4, and 7. SEM images reveal a morphology change from sponge-like platelets to sharp nanowires as the pH increases from 1 to 7. The  $\alpha$ -SnWO<sub>4</sub> thin films were reddish brown in color, and display an indirect band gap of 1.9 eV by diffuse reflectance UV–vis spectroscopy.  $\alpha$ -SnWO<sub>4</sub> is therefore solar-responsive, and a chopped light linear sweep voltammogram recorded under 100 mW/cm<sup>2</sup> AM1.5 simulated solar illumination in a pH 5 0.1 mol/L KP<sub>i</sub> buffer show a visible light response for photoelectrochemical water oxidation, producing 32  $\mu$ A/cm<sup>2</sup> at 1.23 V vs. RHE.

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## 1. Introduction

With an increasing demand and use of energy worldwide, using semiconductors to harness solar energy has been identified as a viable solution for generating chemical fuels [1], both to provide the driving force for transforming water into hydrogen, as well as a means to provide the oxidizing power for large industrial processes, thereby replacing harsh chemical oxidants [2,3]. Many metal oxide semiconductors have been interrogated for their chemical stability, optical properties, and surface catalytic reactivity. For example, TiO<sub>2</sub> ( $E_g = 3.0$  eV) [4], Fe<sub>2</sub>O<sub>3</sub> (2.2 eV) [5], WO<sub>3</sub> (2.7 eV) [6], BiVO<sub>4</sub> (2.4 eV) [7], and CuWO<sub>4</sub> (2.4 eV) [8] are n-type semiconductors that have been studied for oxidative catalysis such as water oxidation. A large emphasis has been placed on using materials with a band gap between 2 eV and 3 eV since this energy encompasses maximum of the solar spectrum (400–800 nm light comprises ~50% of the solar flux that reaches the earth's surface) and accounts for reaction overpotential. For these purposes, we began exploring the optical and electronic properties of  $\alpha$ -SnWO<sub>4</sub> as a thin film electrode.

Despite its calculated band gap of 2.5 eV [9], there are several synthetic challenges for producing  $\alpha$ -SnWO<sub>4</sub> due to the relative

instability of Sn<sup>2+</sup> compared to Sn<sup>4+</sup>. Several groups have produced powder samples of orthorhombic  $\alpha$ -SnWO<sub>4</sub> as well as cubic  $\beta$ -SnWO<sub>4</sub> by calcining in either an inert or vacuum atmosphere as well as by hydrothermal processes [10–12]. Inert or vacuum atmosphere is necessary because Sn<sup>2+</sup> is readily oxidized to Sn<sup>4+</sup> in air. There are examples of forming  $\alpha$ -SnWO<sub>4</sub> by hydrothermal synthesis methods using surfactants under milder, less oxidizing conditions [12,13]. However, these syntheses start from an amorphous precipitate having a 1:1 Sn:W ratio. Therefore synthetic methods with these restrictions become increasingly more complicated when extrapolated to thin film synthesis. The most common technique to produce thin film electrodes is depositing a solution of dissolved precursors onto a conducting substrate, followed by high temperature calcination and annealing. In the case of generating SnWO<sub>4</sub>, the precipitation reaction to generate powder takes place if both precursors are co-dissolved (SnCl<sub>2</sub>(aq) + Na<sub>2</sub>WO<sub>4</sub>(aq) → SnWO<sub>4</sub>(s) + 2NaCl(aq)). Also, solution methods employing WCl<sub>6</sub> and SnCl<sub>2</sub> carried out in organic solvents (*i.e.* ethanol) to control morphology are problematic since combustion of the solvent cannot occur in a reducing or vacuum atmosphere. Herein we demonstrate the first synthetic method to produce phase pure  $\alpha$ -SnWO<sub>4</sub> film electrodes (*i.e.*—not produced from a powder slurry) by a simple hydrothermal method on a fluorinated tin oxide (FTO) transparent conducting substrate without using inert or vacuum atmosphere. This synthesis was accomplished by first synthesizing monoclinic

\* Corresponding author.

E-mail address: [bartmb@umich.edu](mailto:bartmb@umich.edu) (B.M. Bartlett).

WO<sub>3</sub> on FTO and converting it to  $\alpha$ -SnWO<sub>4</sub> in an aqueous SnCl<sub>2</sub> solution.

## 2. Experimental

All reagents were purchased from Sigma Aldrich and used as received with no further purification. FTO films (Pilkington glass) were washed with ethanol and acetone and sonicated for 15 min each. WO<sub>3</sub> was prepared by a known procedure [14]. Sodium tungstate dihydrate, Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O, (0.308 g, 9.34 × 10<sup>2</sup> mmol) was dissolved in 40 mL deionized water. 3 mol/L HCl (13.34 mL, 4 × 10<sup>4</sup> mmol) was added dropwise to the stirring solution, which formed a yellow precipitate. Next, ammonium oxalate, (NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>, (0.267 g, 2.15 × 10<sup>3</sup> mmol) was added and the solution became clear and colorless. An additional 40 mL of deionized water was added, and the solution was stirred for 30 min. Then, 11.5 mL aliquots of solution were transferred to 23 mL PTFE liners (Parr Instrument Company). The FTO films were masked off with PTFE tape to a surface area of 1 cm<sup>2</sup> so that deposition onto the FTO area was controlled. The films were placed face down in the liner and sealed in a stainless steel autoclave. The vessels were held at 120 °C for 12 h with a 10 °C/min ramp rate. These films were either kept as is (WO<sub>3</sub>·H<sub>2</sub>O, yellow/green in appearance) or annealed in air at 450 °C for 1 h (monoclinic WO<sub>3</sub>, green/white in appearance). A 0.5 mol/L SnCl<sub>2</sub> solution was made that had an initial pH of ~1. Next the WO<sub>3</sub>·H<sub>2</sub>O or WO<sub>3</sub> films were placed face down in the hydrothermal vessel filled with 14 mL of 0.5 mol/L SnCl<sub>2</sub> solution whose pH was 1 or adjusted to 4 or 7 with 7 mol/L NaOH and 3 mol/L HCl. The vessels were sealed in steel autoclaves and heated for 24 h at 180 °C with a 10 °C/min ramp rate. The films were rinsed with 3 mol/L HCl to remove any tin chloride hydroxide crystals that formed during the hydrothermal reaction (Fig. S1 in Supporting information). In a control experiment WO<sub>3</sub> films were placed face down in the hydrothermal vessel filled with 14 mL of water adjusted to pH 7 with 7 mol/L NaOH. This control experiment was also carried out in 1 mol/L NaCl to keep the ionic strength of chloride constant in the reaction.

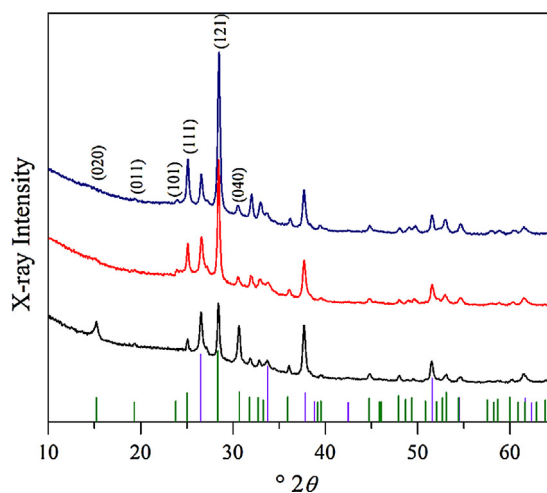
X-ray diffraction patterns were recorded on a Bruker D8 Advance diffractometer equipped with a graphite monochromator, a Lynx-Eye detector, and parallel beam optics using Cu-K $\alpha$  radiation ( $\lambda = 1.54184$  Å). Patterns were collected using a 0.6 mm incidence slit, with a step size and scan rate of 0.04°/step and 0.5 s/step, respectively. Phases were identified as WO<sub>3</sub>·H<sub>2</sub>O (JCPDF 43-0679), WO<sub>3</sub> (JCPDF 72-1465), and SnWO<sub>4</sub> (JCPDF 70-1049) using MDI Jade version 5.0. UV–vis spectra were recorded using a Cary 5000 spectrophotometer (Agilent) equipped with an external diffuse reflectance accessory. Spectra were recorded in reflectance mode, and Tauc plots were then generated using the Kubelka–Munk function,  $F(R) = (1-R)^2/2R$ . Scanning electron microscope images were collected using a FEI Nova Nanolab SEM/FIB with an accelerating voltage of 15 kV.

Photoelectrochemical (PEC) measurements were performed using a custom-built, three-electrode Pyrex glass cell with a quartz viewing window. The cell contained the working thin-film SnWO<sub>4</sub> photoelectrode, an Ag/AgCl reference electrode in saturated KCl (+0.20 V vs. NHE), and a platinum auxiliary electrode. For water oxidation reactions, the supporting electrolyte used was a 0.1 mol/L potassium phosphate buffer (KP<sub>i</sub>) solution at pH 5.00. Electrical contact was made to the FTO substrate by attaching copper wire purchased from Fisher Scientific and using CG Electronics Silver Print II. Electrodes were sealed using Loctite Hysol 1C epoxy. The light source was a Newport-Oriel 150 W Xe arc lamp fitted with a Newport AM 1.5 G filter to simulate incident solar radiation. The lamp power was adjusted to 100 mW/cm<sup>2</sup> using a Newport 1918-R optical power meter equipped with a Newport 818P-015-19 thermopile detector. Voltammetry measurements

were performed with a CH Instruments 660C Electrochemical Workstation.

## 3. Results and discussion

The goal of this work is to synthesize  $\alpha$ -SnWO<sub>4</sub> electrodes using a simple method that excludes the need for an inert or vacuum atmosphere, and avoids adding an annealing step. We synthesized pure  $\alpha$ -SnWO<sub>4</sub> films in aqueous SnCl<sub>2</sub> solution from a previously synthesized monoclinic WO<sub>3</sub> film. The solution did not require deaeration or handling under inert conditions, as all of the synthetic steps were performed aerobically. Orthorhombic WO<sub>3</sub>·H<sub>2</sub>O electrodes were generated by a known hydrothermal synthesis method. This compound is composed of layers of corner sharing octahedrally coordinated WO<sub>5</sub>(H<sub>2</sub>O) units [14]. Corner sharing WO<sub>6</sub> octahedra comprise the structure after annealing, and a hydrothermal method was employed to convert monoclinic WO<sub>3</sub> to red-brown films of  $\alpha$ -SnWO<sub>4</sub> in a subsequent hydrothermal reaction using a 0.5 mol/L solution of SnCl<sub>2</sub> at pH 1, 4 and 7. XRD patterns show the complete conversion to  $\alpha$ -SnWO<sub>4</sub> at each pH (Fig. 1). The *hkl* reflections are shown for low 2 $\theta$  values for the purposes of discussion. The final  $\alpha$ -SnWO<sub>4</sub> product is orthorhombic, but also contains corner-sharing WO<sub>6</sub> octahedra with Sn atoms layered in between, illustrated in Scheme 1. The XRD at pH 1 (black trace Fig. 1) displays a difference in peak intensity for low 2 $\theta$  values compared to pH 4 and 7. Specifically the (0 2 0), (1 1 1), (1 2 1), and (0 4 0) reflections show a change in intensity. Therefore, the preferred orientation or morphology of the film is directed by the pH of the SnCl<sub>2</sub> solution. Converting tungsten oxide hydrate (WO<sub>3</sub>·H<sub>2</sub>O) films to  $\alpha$ -SnWO<sub>4</sub> also occurs under similar conditions at pH 1 (Fig. S2 in Supporting information), 3, 4 and 5 (Fig. S3 in Supporting information). The WO<sub>3</sub>·H<sub>2</sub>O films converted to  $\alpha$ -SnWO<sub>4</sub> at pH 3, 4, and 5 exhibit similar intensities to that of the crystalline WO<sub>3</sub> conversion to  $\alpha$ -SnWO<sub>4</sub> at pH 4 and 7. However, WO<sub>3</sub>·H<sub>2</sub>O films converted to  $\alpha$ -SnWO<sub>4</sub> at pH 1 display similar changes in intensity of *hkl* reflections as seen in the black trace in Fig. 1. The intensities in Fig. S2 are stronger than that of the pH 1 solution for crystalline WO<sub>3</sub>, which is likely due to the fact that the orthorhombic structure is maintained from WO<sub>3</sub>·H<sub>2</sub>O to  $\alpha$ -SnWO<sub>4</sub> as similar reflections appear in the XRD of the WO<sub>3</sub>·H<sub>2</sub>O film before conversion (Fig. S4 in Supporting information).



**Fig. 1.** X-ray diffraction patterns of pure  $\alpha$ -SnWO<sub>4</sub> films. From the bottom to the top the pH of the hydrothermal solution was pH 1 (black), pH 4 (red), and pH 7 (blue). FTO peaks are represented by the violet vertical lines and  $\alpha$ -SnWO<sub>4</sub> is represented by the green vertical lines.

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