



# CuWO<sub>4</sub> films grown via seeding-hydrothermal method for photoelectrochemical water oxidation

Zhen Zhang, Caixia Xiao, Song Li\*

Key Laboratory for Anisotropy and Texture of Materials (MoE), School of Materials Science and Engineering, Northeastern University, Shenyang 110819, China



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## ABSTRACT

Hydrothermal method is widely used to fabricate metal oxide films with various morphology. CuWO<sub>4</sub> is promising photoanode material for photoelectrochemical conversion of light into chemical fuels. In this report, we report that CuWO<sub>4</sub> films on FTO substrate are hydrothermally synthesized by introducing a seeding layer without which only mixed phases of CuO and WO<sub>3</sub> are obtained under the moderate temperature (180 °C) reaction conditions. Photoelectrochemical measurements show that the photoactivity of the CuWO<sub>4</sub> is dependent on the concentration of the hydrothermal solution. Tuning the composition of reaction solution into W-rich resulted WO<sub>3</sub>-CuWO<sub>4</sub> composite film which exhibits much improved photoelectrochemical performance due to enhanced charge separation.

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## 1. Introduction

Photoelectrochemical (PEC) oxidation of water to produce dioxygen is the ideal approach to provide cost-effective electrons for the electrochemical reduction of CO<sub>2</sub> or H<sub>2</sub>O into chemical fuels [1,2]. To meet the energy demand on the terawatt scale, earth abundant elements-based semiconductors with broad sunlight absorption and excellent chemical stabilities are required [3]. Transition metal oxides, which contain a large number of semiconductors with different structures, fulfill the criteria for photoanode. As a n-type semiconductor with suitable band gap of 2.3 eV, CuWO<sub>3</sub> is a promising photoanode candidate and is attracting more and more interests [4,5].

Various methods have been employed to grow CuWO<sub>4</sub> films, including magnetron sputtering [6], atomic layer deposition (ALD) [7], sol-gel method [8], and spray pyrolysis [9]. However, most of these reported synthesis methods involve solid reaction between WO<sub>3</sub> and CuO at high temperatures. For example, T. Hamann synthesized the CuWO<sub>4</sub> film by annealing the stack layers of CuO/WO<sub>3</sub> under 600 °C [7]. In a similar procedure, heating sputtered WO<sub>3</sub> thin film over the CuO nanowire array resulted in nanowire arrays of CuWO<sub>4</sub> nanowire arrays [6]. Direct growth of CuWO<sub>4</sub> on the substrate is still a problem. In addition, film deposition via hydrothermal route attracts intensive interests due to its advantages of simplicity, rapidness, low cost and low process tempera-

ture. In this study, by introducing a seeding layer on the FTO (fluorine-doped tin oxide) substrate, CuWO<sub>4</sub> thin films were prepared by hydrothermal method. By adjusting the ratio of Cu/W in the precursor solution, CuWO<sub>4</sub>-WO<sub>3</sub> composite structure with much enhanced photoelectrochemical performance was obtained.

## 2. Materials and methods

### 2.1. Fabrication of CuWO<sub>4</sub> electrodes

The CuWO<sub>4</sub> films were prepared via two-step method which include seeding layer preparation and subsequent hydrothermal growth. Before the growth, the FTO substrates were washed with acetone, ethanol, and then deionized water in ultrasonic bath. In a typical procedure, cupric chloride and ammonium tungsten hydrate (molar ratio 1:1) were dissolved in ultrapure water to form solution containing a total metal concentration of 0.02 M. 50 μl of the precursor solution were dropped onto the FTO and then dried at 80 °C before heated at 500 °C for 30 min so that a thin seeding layer forms on the FTO. Subsequently, the FTO with seeding layer was put into an autoclave containing 70 vol% of the precursor solution and hold at 180 °C for 5 h.

The obtained products were characterized by X-ray diffraction (XRD) using Cu K<sub>α</sub> as source. The morphology of the film were observed on a scanning electron microscope (SEM) equipped with an X-ray energy-dispersive spectrometer (EDX). The photoelectrochemical water oxidation was carried out in a conventional three-electrode system. The currents were measured using a CHI

\* Corresponding author.

E-mail address: [lis@atm.neu.edu.cn](mailto:lis@atm.neu.edu.cn) (S. Li).

potentiostat (CH Instrument). The illumination with a density of  $0.1 \text{ W/cm}^2$  was provided by a 300 W Xe lamp.

### 3. Results and discussion

Fig. 1 shows the XRD spectra of hydrothermally synthesized samples before and after calcination at  $500^\circ\text{C}$ . Only diffraction peaks related to the FTO substrate were obvious in spectra of hydrothermally grown film. Diffraction peaks that can be ascribed to  $\text{CuWO}_4$  appear when the film was calcined at  $500^\circ\text{C}$  for 2 h. To further understand the growth process of the film, powders precipitated in the bulk solution were collected to observe the phase transformation. As shown in Fig. 1(d), the powders are composed of hexagonal  $\text{WO}_3$  (PDF card no. 75-2187) and  $\text{CuO}$  and no sign of  $\text{CuWO}_4$  is present, suggesting that a kinetic barrier [11] for the formation of  $\text{CuWO}_4$  structure exists under the hydrothermal conditions though the process is thermodynamically favorable. Also, the broadened diffraction peaks of the spectrum demonstrate the low crystallinity of the powders which may be a result of insufficient hydrothermal temperature or severe inter-doping of the two metals into the other oxide [10]. The atomic ratio between Cu and W determined by the ICP (inductively coupled plasma) measurements is 1. Heating treatment at  $500^\circ\text{C}$  for 2 h converts these mixed oxides into pure  $\text{CuWO}_4$  phase, as shown in Fig. 1(c) with the standard pattern as reference.

To overcome the growth barrier, a seeding layer which could assist the nucleation of  $\text{CuWO}_4$  [12,13] is introduced by dipping the FTO substrate into the solution containing 0.01 mol/L Cu and W precursors and then annealed at  $500^\circ\text{C}$  for 1 h in the air. Hydrothermal treatment of these seeded substrate in solutions containing 0.01, 0.02, and 0.05 M precursors produced well-crystallized  $\text{CuWO}_4$ , as shown in Fig. 2. However,  $\text{WO}_3$  structure is also found in film prepared in 0.05 M, suggesting that the growth

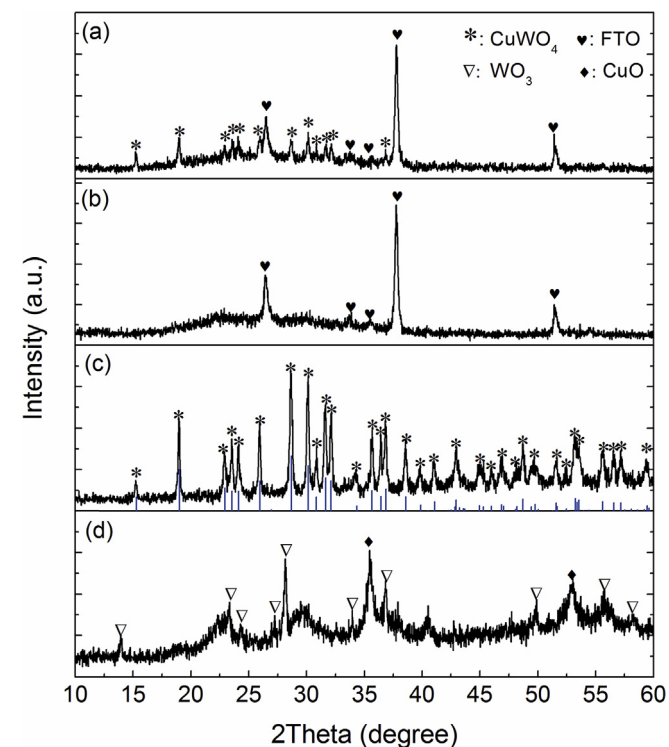


Fig. 1. XRD spectra of single-step hydrothermally synthesized films (a–b) and concurrently obtained powders (c–d). (a, c) After calcination at  $500^\circ\text{C}$  for 2 h; (b, d) as-hydrothermal prepared before calcination.

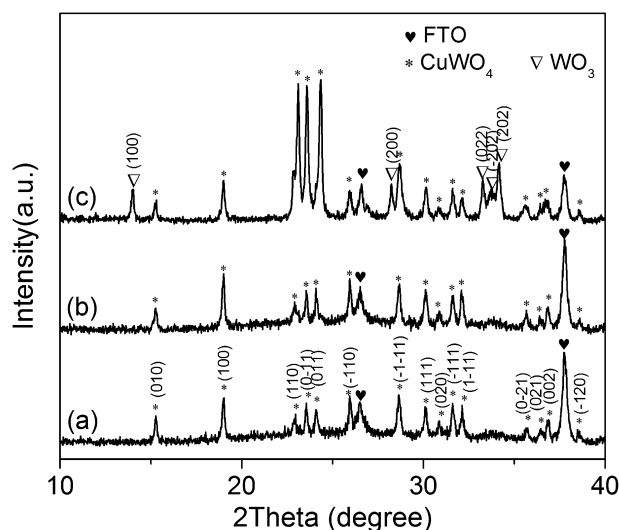


Fig. 2. XRD spectra of films hydrothermally grown on seeding-pretreated FTO substrate in solutions containing different concentrations of Cu and W precursors. (a) 0.01 M; (b) 0.02 M; (c) 0.05 M.

kinetics of  $\text{WO}_3$  is superior to the  $\text{CuWO}_4$ . The SEM morphology (Fig. 3) shows that the hydrothermal synthesized  $\text{CuWO}_4$  films are dense and are composed of small crystals below 100 nm.

Photocurrent density vs applied potential plots were measured to evaluate the photoelectrochemical dependence of the as-prepared films on the hydrothermal conditions, as shown in Fig. 4. The  $\text{CuWO}_4$  films prepared by the seeding-hydrothermal two step method exhibited photoactivity for PEC water oxidation, with photocurrent onset potential around  $0.62 \text{ V vs RHE}$ . The photocurrent densities increased from  $11.6 \mu\text{A/cm}^2$  to  $43.3 \mu\text{A/cm}^2$  at  $1.4 \text{ V vs RHE}$  along with the total concentration of (Cu + W) in the hydrothermal solution increasing from 0.01 M to 0.02 M, as shown in Fig. 4(a–c). The enhancement can be ascribed to thicker film deposited at higher precursor concentration, so that more electron-hole pairs could be created. The onset potentials are much more cathodic than widely investigated hematite [14], implying its great potential of building tandem photoelectrolysis cells with lower bandgap semiconductors such as silicon [15]. Moreover, when more tungsten is present in the reaction (molar ratio of W: Cu = 1.05), the resulted photoanode yields much higher photocurrent density which reaches  $1.57 \text{ mA/cm}^2$  at  $1.4 \text{ V vs RHE}$ . The photocurrent density in this work exceeds many reported values for  $\text{CuWO}_4$  which are generally at the level below  $1 \text{ mA/cm}^2$  [4,7]. The enhancement could be due to the formation of  $\text{WO}_3$ - $\text{CuWO}_4$  local heterostructures [16,17] and high-crystallinity under hydrothermal conditions.

Fig. 4(B) schematically illustrates the relative band edge positions of  $\text{CuWO}_4$  and  $\text{WO}_3$  which helps the understanding promoting effects of  $\text{WO}_3$ . The band gap of  $\text{CuWO}_4$  is narrower than that of  $\text{WO}_3$  because of the orbital mixing between  $\text{O}(2p)$  and  $\text{Cu}(3d)$  [4]. The presence of  $\text{WO}_3$  impurities hydrothermally grown in W-rich solution form heterojunctions to surrounding  $\text{CuWO}_4$  crystals. The mismatch of the band edge improves the separation of photo-generated electron-hole pairs [18,19]. In particular, the photo-generated electrons in the  $\text{CuWO}_4$  are injected into the  $\text{WO}_3$ , so that the surface recombination, which has been proven to be a major cause for low PEC performance of many photoanodes [1,20,21], is reduced. In Fig. 4(A), the onset potential of the photocurrent remains unchanged after the formation of the heterojunctions, suggesting that the oxidation reactions of water with photogenerated holes occur over the  $\text{CuWO}_4$  surface.

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