



Article Improved Charge Separation in WO₃/CuWO₄ Composite Photoanodes for Photoelectrochemical Water Oxidation

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Academic Editor: Deepak Pant

Received: 3 March 2016; Accepted: 29 April 2016; Published: 7 May 2016

Abstract: Porous tungsten oxide/copper tungstate (WO₃/CuWO₄) composite thin films were fabricated via a facile *in situ* conversion method, with a polymer templating strategy. Copper nitrate (Cu(NO₃)₂) solution with the copolymer surfactant Pluronic[®]F-127 (Sigma-Aldrich, St. Louis, MO, USA, generic name, poloxamer 407) was loaded onto WO₃ substrates by programmed dip coating, followed by heat treatment in air at 550 °C. The Cu²⁺ reacted with the WO₃ substrate to form the CuWO₄ compound. The composite WO₃/CuWO₄ thin films demonstrated improved photoelectrochemical (PEC) performance over WO₃ and CuWO₄ single phase photoanodes. The factors of light absorption and charge separation efficiency of the composite and two single phase films were investigated to understand the reasons for the PEC enhancement of WO₃/CuWO₄ composite thin films. The photocurrent was generated from water splitting as confirmed by hydrogen and oxygen gas evolution, and Faradic efficiency was calculated based on the amount of H₂ produced. This work provides a low-cost and controllable method to prepare WO₃-metal tungstate composite thin films, and also helps to deepen the understanding of charge transfer in WO₃/CuWO₄ heterojunction.

Keywords: CuWO₄; WO₃; composite thin film; charge separation; photoelectrochemical water splitting

1. Introduction

In recent years, photoelectrochemical (PEC) water splitting has aroused tremendous research interest due to its sustainable and carbon neutral attributes for producing high energy density fuels [1–4]. A visible light active photoanode which utilizes more of the solar spectrum is highly desirable, and thus the earth-abundant α -Fe₂O₃ (band gap 2.1 eV) and WO₃ (band gap 2.6 eV) have become popular candidates for water oxidation. Due to the intrinsic long-range antiferromagnetic order in α -Fe₂O₃, it has a short hole diffusion length (2–20 nm) [5,6] and low charge-carrier mobility ($10^{-2}-10^{-1} \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$) [7]. In comparison, WO₃ has a much longer hole diffusion length (150 nm) and higher mobility ($10 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{S}^{-1}$) [8,9]. Nevertheless, its limited utilization of the visible light

spectrum and its chemical instability in neutral electrolyte call for further improvement of WO_3 for use as photoanode material [10–12].

Copper tungstate (CuWO₄) has recently been recognized as a promising tungsten-based ternary oxide for PEC water oxidation [9,13–20]. It is an n-type semiconductor with a smaller band gap of 2.3 eV, corresponding to a theoretical photocurrent density (J_{max}) of 10.7 mA/cm² [18,21,22]. In addition, CuWO₄ is stable in neutral pH electrolyte, because of the hybridization of Cu-d orbitals with O-p orbitals leading to higher chemical stability due to strong metal-oxo bonds [9,16,23,24]. Recently, several studies reported on the preparation of single phase of CuWO₄ photoelectrodes and evaluation of their PEC properties for water oxidation. For example, CuWO₄ thin films prepared by electro-deposition shows a photocurrent density of 0.20 mA/cm² in a linear sweep test at the applied bias of 1.23 V *vs.* reversible hydrogen electrode potential (V_{RHE}) in pH 7 potassium phosphate buffer solution [9]. CuWO₄ formed by addition of excessive amounts of Cu(NO₃)₂ solution onto porous WO₃ thin film followed by annealing exhibited approximately 0.15 mA/cm² at 1.23 V_{RHE}, and good stability in pH 7 (phosphate) and pH 9 (borate buffer) solutions [20]. CuWO₄ thin films prepared by co-sputtering Cu and W metals on FTO glass displayed a photocurrent density of 0.20 mA/cm² at 1.23 V_{RHE} [25].

However, the empty orbital of $Cu(3dx^2-y^2)$ in pure $CuWO_4$ is detrimental to charge transfer in the pure phase [16]. Therefore, fabrication of $CuWO_4$ -based composites or heterojunction photoanodes is needed to improve its charge transfer properties. For example, $CuWO_4$:WO₃ composite electrode fabricated by simultaneous electrochemical deposition with $CuWO_4$:WO₃ at a 1:1 ratio can oxidize water at a faster rate than pure $CuWO_4$ electrode of similar thickness [15]. Another $CuWO_4/BiVO_4$ heterojunction photoanode prepared by spray-coating a Bi:V (1:1) precursor solution onto electrodeposited $CuWO_4$ thin film led to a nearly 1.8-fold increase of the photocurrent density compared to pure $CuWO_4$ [16]. Solid solution electrodes of $CuWO_4$: $CuMoO_4$ ($CuW_{1-x}Mo_xO_4$) were synthesized by simultaneous electrochemical deposition of $CuWO_4$ and $CuMoO_4$ with different W:Mo ratios. These solid solution electrodes exhibited enhanced photocurrent and the incident photon-to current efficiency (IPCE) compared with pure $CuWO_4$, which is possibly due to the lowered conduction band edge caused by the presence of molybdenum atoms, thus leading to a reduced band gap [26]. In addition, noble metals such as gold and silver nanoparticles when mixed in $CuWO_4$ film increase the speed of charge transfer in the thin films [27,28].

As Cu^{2+} can react with WO₃ to form CuWO₄ during high temperature annealing [20], it is possible to fabricate WO₃/CuWO₄ composite or heterojunction thin films with controlled addition of Cu²⁺ precursor onto WO₃ substrate. There are a few recent studies on the preparation of WO₃/CuWO₄ composite thin films [29–31], but quantitative analysis of light absorption and charge separation efficiency and definite experimental evidence of PEC gas evolution remain elusive.

In this paper, we prepared WO₃/CuWO₄ heterojunction thin film via a facile *in situ* conversion method. Controllable loading of CuWO₄ could be achieved with different runs of dip coating. Moreover, with the addition of organic surfactant F127, the formed CuWO₄ layer contained interconnected porous nanostructures. These WO₃/CuWO₄ films showed enhanced PEC performance over individual WO₃ or CuWO₄. By decoupling the photo absorption and charge transfer processes, it is shown that WO₃/CuWO₄ heterojunction thin films exhibit enhanced efficiency in each process because of the narrower band gap of CuWO₄, and favorable band alignment between WO₃ and CuWO₄. Electrochemical impedance spectroscopy indicated a reduced charge transfer resistance for the composite thin film under AM1.5 illumination with 1.2 V_{RHE} bias. Further, H₂ and O₂ evolution test was undertaken, and the photocurrent generated from water splitting was confirmed by the detection and quantification of the product gases. This *in situ* conversion strategy can be used to fabricate other porous WO₃/metal tungstate composite thin films. Our results also provide some reference for designing photoanodes with higher efficiency.

2. Results and Discussion

2.1. Synthesis and Characterization of Pristine WO₃ and WO₃/CuWO₄ Composite Thin Films

In this report, three representative samples with 0, 4 and 8 runs of programmed dip coating of Cu²⁺ solution are discussed, which gave rise to WO₃, WO₃/CuWO₄ composite and CuWO₄ materials respectively. XRD patterns in Figure 1 indicate that the WO₃ thin films obtained from magnetron sputtered metallic W thin film are of the monoclinic phase (JCPDS No. 43-1035), which is the most photocatalytically active phase for water oxidation [10]. For comparison, we also sputtered metallic W onto a normal glass slide, which produced the orthorhombic phase of WO₃ hydrate (JCPDS No. 35-0270) [10], to the contrary, as shown in XRD patterns in Figure S1. It is thus believed that the crystalline layer of F:SnO₂ helped with the formation of monoclinic phase of WO₃. Thin films of WO₃/CuWO₄ and CuWO₄ showed the characteristic peaks of CuWO₄ (JCPDF 72-0616) [9]. UV-Vis/DRS results of the three samples are shown in Figure 1b. Pristine WO₃ absorbs light up to 464 nm, which is in accordance with the band gap of about 2.7 eV of monoclinic WO₃. The light absorption of CuWO₄ extends to 540 nm, corresponding to the smaller band gap of CuWO₄ (2.3 eV).



Figure 1. XRD patterns (**a**) and UV-Vis absorption spectrum (**b**) of pristine WO₃, WO₃/CuWO₄, and CuWO₄ thin films.

The top and cross-section views of all the films observed by field emission scanning electron microscope (FESEM) are shown in Figure 2. A summary of the average thickness of WO₃ and CuWO₄ of each sample is provided in Table 1. Figure 2a,b shows the images of pristine WO₃. The WO₃ thin film was composed of densely assembled WO₃ nanoparticles of irregular shape around 50–90 nm in diameter, and the average thickness of film was around 415 nm. Figure 2c,d are the images of WO₃/CuWO₄ composite thin film, with a porous layer of CuWO₄ particles uniformly grown on the WO₃ substrate. The thickness of WO₃ layer was greatly reduced to 150 nm due to the *in situ* reaction with Cu²⁺ ions to form CuWO₄. The transmission electron microscope (TEM) image of the scraped particles from the composite film in Figure S2 displays a network-like structure in the thin film, corresponding to the porous CuWO₄ nanostructure in FESEM observation. In Figure 2e,f, with further increased loading of Cu²⁺ ions, the WO₃ film was completely consumed, forming a porous layer of CuWO₄ 1 µm thick.



Figure 2. FESEM images of top and cross-section views of WO₃ (**a**,**b**); WO₃/CuWO₄ composite (**c**,**d**) and CuWO₄ (**e**,**f**) thin films.

Table 1. Summary of the thickness of the WO₃ and CuWO₄ layers of the three samples.

Sample	Thickness of WO ₃ (nm)	Thickness of CuWO ₄ (nm)
Pristine WO ₃	415	0
WO ₃ /CuWO ₄	150	600
CuWO ₄	0	1000

2.2. Photoelectrochemical Performance of Thin Films

The pristine WO_3 , $WO_3/CuWO_4$, and $CuWO_4$ thin films were used as photoanodes in a conventional three-electrode setup. Their PEC performance was investigated by measuring the photocurrent with back-illumination as shown in Figure 3. In the linear sweep voltammetry (LSV) results in Figure 3a, all the samples exhibited negligible photocurrent under dark condition. Composite thin films obtained from different runs are provided in Figure S3. At 1.20 V_{RHE} , bare WO_3 and $CuWO_4$ were of very similar photocurrent density, and $WO_3/CuWO_4$ (0.45 mA/cm²) showed a current density more than two times higher than WO₃ and CuWO₄ electrodes. As shown in the supporting information (Figure S3), all the composite thin films demonstrate higher photocurrent compared to single component thin films. The relatively low photocurrent of the WO_3 underlayer in our report could be due to the preparation condition and insufficient thickness. As we annealed the tungsten film in air to let it oxidize into WO₃, the insertion of oxygen atoms will make the thin film expand. As a result, the back contact with fluorine doped tin oxide (FTO) could be adversely affected. In addition, the annealing temperature and time can also affect the oxygen vacancies and carrier density, which will subsequently influence the photocurrent of WO₃ films. However, when a thin layer of WO₃ was coupled with CuWO₄, the photocurrent of the composite film was remarkably improved compared with the single phase. Figure 3b shows the on-off photocurrent profile of the composite WO₃/CuWO₄ under a constant bias of 1.20 V_{RHE}, recorded over a duration of 600 s with interval of 5 s. The composite thin film showed a constant photocurrent though transient spikes were spotted for both samples, which could be caused by the surface-trapped photo-generated minority carriers which recombine with the photo-generated major carriers [32]. Figure 3c shows the IPCE curves for WO₃, WO₃/CuWO₄ and CuWO₄ electrodes measured at 1.20 V_{RHE}. The WO₃/CuWO₄ composite thin films had much higher IPCE values compared with WO₃ and CuWO₄ films. Though light absorption of CuWO₄ covered the wavelengths up to 540 nm, the identical wavelength ranges of the three thin films in the IPCE curves indicate that the charge carriers generated in CuWO₄ in the wavelength range 470–540 nm make little contribution to photocurrent generation [29,31]. The simulated photocurrents in Figure 3d for all samples were also calculated by integrating the IPCE spectra with a standard AM 1.5 G solar spectrum from Equation (1). The simulated photocurrent is independent of the light source and applied filters, and thus it is more accurate in evaluation of the PEC performance of the thin films. The values obtained were reasonable compared to measured photocurrents.

$$I_{\text{simulated}} = \int_{350}^{550} \left(IPCE\left(\lambda\right) \times \Phi\left(\lambda\right) \times e\right) d\lambda \tag{1}$$

where λ is the wavelength of light in unit of nm and IPCE (λ) is measured and calculated as will be described in Experiment Section 3.5. $\Phi(\lambda)$ is the photon flux of sunlight in photons/m²/s. The photon flux can be measured from tabulated solar irradiance data, $E(\lambda)$, via $\Phi(\lambda) = E(\lambda)/(1240/\lambda)$ [33].



Figure 3. (a) Linear sweep voltammetry of WO₃, WO₃/CuWO₄ and CuWO₄ electrodes (solid lines: photocurrent under AM 1.5G illumination, dashed lines: dark current); (b) Photocurrent stability of WO₃/CuWO₄ electrode at 600 s; (c) IPCE measurement of WO₃, WO₃/CuWO₄, and CuWO₄ electrodes (note: IPCE was done using back illumination which is in accordance with photocurrent-potential measurement); (d) Integrated photocurrent based on the IPCE data (350–550 nm), solar photon flux is shown as a reference. (**a**–**c**) were tested in 0.5 M of Na₂SO₄ aqueous solution with illumination of AM 1.5; and (**b**,**c**) had 1.20 V_{RHE} bias applied to the electrodes.

In order to measure the band structures of WO_3 and $CuWO_4$, the Mott-Schottky measurement is shown in Figure 4a,b, and the result for $WO_3/CuWO_4$ composite thin film is shown in Figure S4. Given the band gap measured from UV-Vis absorption, the band structures of WO_3 and $CuWO_4$ are shown in Figure 4c. The conduction band of CuWO₄ is located at +0.2 eV (*vs.* normal hydrogen electrode, NHE) and that of WO₃ is located at +0.4 eV (*vs.* NHE), while valence band of CuWO₄ is at +2.4 eV (*vs.* NHE), lower than that of WO₃ at +3.0 eV (*vs.* NHE). Therefore, these two components can form a heterojunction pair, and photo-generated holes from the inner WO₃ layer will be transferred to the outer layer of CuWO₄ in WO₃/CuWO₄ composite electrode.



Figure 4. Mott-Schottky plots of WO₃ thin film (**a**); and CuWO₄ thin film (**b**) at 10 k and 5 k Hz under dark conditions; (**c**) Band structure of WO₃ and CuWO₄; (**d**) Nyquist plots of WO₃, WO₃/CuWO₄, and CuWO₄ thin films under AM 1.5 illumination in 0.5 M Na₂SO₄ with 1.20 V_{RHE} applied bias.

The carrier density can be calculated by

$$\frac{1}{C_{SC}}^2 = \frac{2}{e\epsilon\epsilon_0 N_D} (E - E_{fb} - \frac{K_b T}{e}) \tag{2}$$

where C_{SC} , q, ε_0 , ε , N_D, and E_{fb} are capacitance, the electron charge, permittivity in vacuum, dielectric constant, donor carrier density and flat-band potential of the semiconductor, respectively. Using Equation (2), the carrier densities are 1.73×10^{19} for WO₃ and 3.36×10^{18} for CuWO₄. Our low carrier density is possibly due to the synthesis method for the thin films. The literature has shown that annealing in air can affect both the oxygen vacancies and the types of other vacancies/defects within a nanostructured thin film [28].

Electrochemical impedance spectroscopy (EIS) measurements were carried out to evaluate the overall resistance of the three photoanodes, and is shown in Figure 4d under illumination and 1.2 V_{RHE} bias. The semicircle in the medium-frequency region was attributed to the charge-transfer process. The diameter of the WO₃/CuWO₄ semicircle was the smallest among the three electrodes, which was in accordance with the LSV results [16,25]. CuWO₄ had the largest semicircle diameter, indicating a very high charge transfer resistance in the thin film, which was possibly related to the poor intrinsic charge transfer property of CuWO₄. However, when CuWO₄ was coupled with WO₃ to form a

2.3. Comparison of Absorption Efficiency (η_{abs}), and Charge Separation Efficiency (η_{sep}) of WO₃, CuWO₄ and WO₃/CuWO₄ Thin Films

Since the WO₃/CuWO₄ electrode demonstrated remarkable improvement in photoelectrochemical and EIS measurement compared with pristine WO₃ substrate and CuWO₄ films, we further extracted the efficiency values of light absorption (η_{abs}) and charge separation (η_{sep}) based on Equations (3) and (4) to quantify the contribution of each factor [34,35].

$$J_{abs} = \int_{350}^{550} (\eta_{abs} \times \Phi(\lambda) \times e) d\lambda$$
(3)

$$\eta_{sep} = J_{sca}/J_{abs} \tag{4}$$

where J_{abs} is the photo current density calculated by multiplying η_{abs} by the standard AM 1.5 G (100 mW/cm²) solar spectrum, $\Phi(\lambda)$ is the photon flux of sunlight in photons/m²/s, e is the charge of an electron (C). J_{sca} is the photocurrent of the photoelectrode in the presence of scavengers as a function of applied bias.

By measuring the light transmittance and reflectance in an integrated sphere (see Figure S5), we were able to obtain the η_{abs} of pristine WO₃, CuWO₄ and WO₃/CuWO₄ in Figure 5a. It shows that more photons can be absorbed in the presence of CuWO₄. With the measured values of η_{abs} and Equation (1), the integrated J_{abs} over the AM 1.5 spectrum of pristine WO₃, CuWO₄ and WO₃/CuWO₄ films are 1.8, 4.7 and 3.2 mA/cm², respectively. The charge separation efficiency (η_{sep}) can be determined by adding the hole scavenger H₂O₂ to the electrolyte. The presence of H₂O₂ increased photocurrent density of all the three thin films (Figure S6), which was due to the much faster charge transfer rate promoted by the hole scavenger. According to Equation (4), charge separation (η_{sep}) efficiency of the three films was obtained and shown in Figure 5b. The composite WO₃/CuWO₄ thin film showed significant improvement of charge separation efficiency compared with CuWO₄ film. This indicates that with a thin underlayer of WO₃, the charge separation characteristics of CuWO₄ are greatly enhanced, which leads to much higher photocurrent.



Figure 5. (a) Light absorption efficiency of WO₃, CuWO₄ and WO₃/CuWO₄ films obtained from an integrating sphere; (b) Charge separation efficiency of WO₃, CuWO₄ and WO₃/CuWO₄ electrodes.

2.4. Photoelectrochemical Water Splitting

In order to confirm that photocurrent was generated by water splitting, we conducted hydrogen and oxygen evolution under AM 1.5 illumination with 1.20 V_{RHE} in 0.5 M Na₂SO₄ electrolyte. Figure 6a illustrates how the charge carriers are transported in the WO₃/CuWO₄ composite photoanode. Both WO₃ and CuWO₄ are excited by back illumination and generate charge carriers. Holes from WO₃ are transferred to CuWO₄ due to the formation of heterojunction, and are injected into the electrolyte from porous CuWO₄ surface to oxidize water into O₂. Electrons are directed to the Pt electrode where water molecules are reduced to hydrogen gas. As shown in Figure 6b, the total amount of oxygen and hydrogen evolved in three hours is about 5.0 and 14.0 µmol, respectively. The ratio of H₂ to O₂ produced is greater than the stoichiometric ratio [36]:

Faradaic Efficiency (FE)
$$\%$$
 = actual hydrogen evolution rate/calculated amount
from photocurrent generation \times 100 (5)

which was about 79% using the hydrogen quantity calculated according to Equation (5). The loss of faradaic efficiency was possibly due to the slow kinetics of water oxidation and back reaction of H_2 and O_2 . The 3 h time course photocurrent density is presented in the inset of Figure 6b. The photocurrent dropped to around 63% of the initial current density within the first hour, but we believe that the stability of $WO_3/CuWO_4$ photoanode could be improved by loading oxygen evolution reaction (OER) co-catalyst on the electrode surface.



Figure 6. (a) Illustration of working mechanism of $WO_3/CuWO_4$ composite photoanode; and (b) hydrogen and oxygen evolution by $WO_3/CuWO_4$ photoanode under AM 1.5 illumination in 0.5 M Na₂SO₄ at bias of 1.20 V_{RHE}. The expected amount of hydrogen gas, $e^-/2$ is also provided for evaluation of Faradaic efficiency. Inset graph shows the time course of photocurrent generation in 3 h.

3. Materials and Methods

3.1. Preparation of W Thin Film from Magnetron Sputtering

The synthesis route of the WO₃/CuWO₄ film is shown in Scheme 1. Tungsten film was deposited onto F-doped tin oxide (FTO) glass (sheet resistance $\leq 15 \Omega$ /square, size: 10 mm × 25 mm and thickness: 2.2 mm) using direct current (DC) magnetron sputtering. The FTO glass was cleaned using acetone, ethanol and DI water prior to the sputtering. A metallic tungsten target (W, 3.00'' diameter × 0.250'' thick, 99.95% purity, Kurt J. Lesker, Jefferson Hills, PA, USA) was used as the sputtering target. The distance between the target and the substrate was set at around 10 cm. The sputtering chamber was evacuated to 8.0×10^{-6} Torr or lower using a rotary pump and a turbo pump before introducing argon gas. The argon flow rate was kept constant at 20 sccm. A manual gate valve was used to fix the pressure inside the sputtering chamber at 20.0 mTorr during film deposition. The surface of the target was cleaned by sputtering the W target for 10 min before deposition onto FTO glass. The whole sputtering process lasted for 5.0 min at a constant working power of 230 W to obtain the black metallic W thin film.



Scheme 1. Preparation of FTO/W, FTO/WO₃, FTO/WO₃/Cu²⁺ and FTO/WO₃/CuWO₄ thin films.

3.2. Fabrication of WO₃ Thin Film

The as-prepared metallic W thin film was placed in a clean porcelain crucible, and was transferred to a muffle furnace (CWF 12/5, Carbolite, Derbyshire, UK). The thin film was calcined at 500 °C for 2 h with a ramping rate of 2 °C/min for heating step and was cooled down naturally. Monoclinic WO₃ thin film with a light yellow colour was obtained.

3.3. Fabrication of WO₃/CuWO₄ Thin Films

0.2 M of copper nitrate trihydrate (Cu(NO₃)₂·3H₂O, Sigma-Aldrich, St. Louis, MO, USA) ethanol solution with 0.04 g/mL of Pluronic[®] F-127 (Sigma-Aldrich, St. Louis, MO, USA) was prepared as the dip coating solution. The FTO/WO₃ was installed on dip coater (KSV NIMA), with insertion and withdrawal speed of 100 mm/min and 30 s submerge duration in Cu(NO₃)₂·3H₂O ethanol solution. The process was repeated for 4 and 8 runs to load different amount of Cu²⁺ ions. The films were subsequently heated in air at 550 C for 4 h in a muffle furnace, with a ramping rate of 2 °C/min for both heating and cooling steps. After annealing, the colour of the thin film changed to bright yellow, indicating the formation of a layer of CuWO₄ during heat treatment. CuO that formed from decomposition of excess Cu(NO₃)₂ along the edges of WO₃ thin film and FTO glass during heating was dissolved away by soaking in a 0.5 M HCl solution for 10 min.

3.4. Material Characterization

X-ray diffraction (XRD) patterns of all the thin films were recorded using XRD-6000 X-ray diffractometer (Shimadzu, Kyoto, Japan) with Cu K α radiation (λ = 0.15418 nm). The surface morphology was analyzed by FESEM (JSM-7600F, JEOL, Tokyo, Japan). The morphology of CuWO₄ nanoparticles were observed using TEM (JEM-2010, JEOL, Tokyo, Japan).UV-Vis/DRS of thin films was recorded using a Varian Cary 5000 UV-Vis spectrophotometer (Varian/Agilent, Santa Clara, CA, USA), with BaSO₄ as a reference. Absorption efficiency (η_{abs}) of thin films was determined by measuring transmission and reflection spectra using integrating sphere (Absorbance = 1 – Transmittance – Reflectance) [37].

3.5. Photoelectrochemical (PEC) Measurement

To investigate the photoelectrochemical properties of WO₃, WO₃/CuWO₄, and CuWO₄ photoanodes, a conventional three-electrode system was used. All the PEC measurements were carried out in a home-made Teflon PEC cell with an illumination window of 5 mm inner diameter for back-illumination. The surface area of electrode exposed under illumination was about 0.2 cm². 0.5 M of sodium sulphate (Na₂SO₄, Sigma-Aldrich, St. Louis, MO, USA) in deionized water solution with a pH value of 6 was used as the electrolyte. Platinum (Pt) coil and silver/silver chloride (Ag/AgCl)

were used as counter and reference electrodes, respectively. The prepared thin films were used as working electrodes. The light source was simulated sunlight from a 150 W xenon solar simulator (67005, Newport Corp., Irvine, CA, USA) through an Air Mass filter (AM 1.5, Global, 81094, Newport Corp., Irvine, CA, USA) with a constant light intensity to standard AM1.5 sunlight (100 mW/cm²) at the photoanode surface. Linear sweep voltammetry (LSV) was carried out by an electrochemistry workstation (CHI 852C, CH Instruments, Shanghai, China) both in dark and under AM1.5 sunlight simulator. Stability of $WO_3/CuWO_4$ sample was carried out at a bias potential of 1.20 V_{RHE} for 600 s with illumination on-off interval of 5 s. Charge separation efficiency was obtained by measuring light absorption of thin films and photocurrent in $0.5 \text{ M Na}_2\text{SO}_4 + 0.5 \text{ M H}_2\text{O}_2$ aqueous solution. Incident photon to electron conversion efficiency (IPCE) was measured with a xenon light source (66983, Newport Corp., Irvine, CA, USA) coupled with a monochromator (74125, Newport Corp., Irvine, CA, USA) at a bias of 1.20 V_{RHE} from back illumination. A Si photodiode (DH-Si, Bentham, Reading, Berkshire, UK) with known IPCE was used to calculate the IPCE of prepared thin films. A source meter (Keithley Instruments Inc., Solon, OH, USA, Model: 2400) was used to record the photocurrent of Si diode. CHI 852C electrochemistry workstation was used to record the photocurrent of each photoanode. IPCE calculation is given in the following formula:

$$IPCE(\lambda) = 100 \times 1240 \times (J(\lambda) - J_{dark}) / \lambda / I(\lambda) [38]$$
(6)

where λ is the wavelength of light in unit of nm; J(λ) is the photocurrent density in mA/cm² under illumination at λ ; J_{dark} is the photocurrent density measured at dark; and I(λ) is the incident light intensity in mW/cm² at λ [38].

Electrochemical impedance spectroscopy (EIS) was performed using an Autolab PGSTAT 302N system (Metrohm Autolab, Utrecht, The Netherlands) equipped with the FAR2 Faraday impedance module (Metrohm Autolab, Utrecht, The Netherlands). The flat band potential of CuWO₄ was determined using the Mott-Schottky equation on a CuWO₄ sample at frequencies of 5 k and 10 k Hz. The Nyquist plot was measured at 1.20 V_{RHE} with a frequency ranging from 0.01 Hz to 100 kHz at 10 mV amplitude potential under AM1.5 illumination.

3.6. Photoelectrochemical Water Splitting

The photoelectrochemical water splitting was carried out in an air-tight reactor using back illumination. The light source (AM 1.5 sunlight, 100 mW/cm²) and applied bias 1.20 V_{RHE} were kept the same during the measurement. The amount of hydrogen and oxygen was analyzed by a gas chromatographer (GC-7890A, Agilent, Agilent, Santa Clara, CA, USA) equipped with thermal conductivity detector (TCD) detector.

4. Conclusions

In conclusion, we have converted monoclinic WO₃ thin film into WO₃/CuWO₄ composite and CuWO₄ films through a facile dip-coating step followed by heat treatment. The PEC and EIS measurements showed that the presence of a thin layer of WO₃ beneath CuWO₄ can enhance the photocurrent density and reduce the charge transfer resistance compared with pure CuWO₄ film. By separately studying the photo absorption and charge transfer efficiencies, it was demonstrated that the WO₃/CuWO₄ composite film exhibited enhancements in each process compared with single-phase WO₃ and CuWO₄. Hydrogen and oxygen evolution was conducted to confirm that the photocurrent was generated from water splitting. Our result has provided a low-cost and controllable method to prepare WO₃-metal tungstate heterojunction thin films, and helped to provide a reference for designing CuWO₄-based photoanodes with greater efficiency.

Supplementary Materials: The following are available online at www.mdpi.com/1996-1944/9/5/348/s1. Figure S1: XRD patterns of different WO₃ phases obtained from magnetron sputtering on FTO (red) and normal glass slide (blue) substrates, which showed the FTO layer helped to induce the crystal growth of monoclinic WO₃.

Figure S2: TEM images of particles scraped from WO₃/CuWO₄, indicating network morphology of the CuWO₄ layer. Figure S3: Photocurrent comparison of thin film obtained from different runs of dip coating. Figure S4: Mott-Schottky plots of WO₃/CuWO₄ thin film at 10 k and 5 k Hz under dark conditions. Figure S5: Absorption efficiency of the WO₃, CuWO₄ and WO₃/CuWO₄ thin film by measuring the transmission and reflection spectra using an integrating sphere (Absorbance (η_{abs}) = 1 – Transmittance – Reflectance). Figure S6: Linear sweep voltammetry of all samples with (solid lines) and without the illumination of AM 1.5 (dashed lines), measured in 0.5 M Na₂SO₄ + 0.5 M H₂O₂ aqueous solution.

Acknowledgments: This research project is funded by the National Research Foundation (NRF), Prime Minister's Office, Singapore under its Campus for Research Excellence and Technological Enterprise (CREATE) program.

Author Contributions: Danping Wang, Lydia Helena Wong and Zhong Chen primarily designed the experiments. Danping Wang, Prince Saurabh Bassi, Huan Qi, Xin Zhao and Gurudayal carried out the experiments and material characterizations. Danping Wang, Prince Saurabh Bassi, Xin Zhao and Gurudayal analyzed the experiment results. Danping Wang wrote the manuscript with the input from Zhong Chen, Lydia Helena Wong, Rong Xu and Thirumany Sritharan.

Conflicts of Interest: The authors declare no conflict of interest.

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