

Article

Fabrication and Characterization of P-Type Semiconducting Copper Oxide-Based Thin-Film Photoelectrodes for Solar Water Splitting

Chih-Jui Chang ^{1,†}, Chih-Wei Lai ^{1,†}, Wei-Cheng Jiang ¹, Yi-Syuan Li ¹, Changsik Choi ^{2,*}, Hsin-Chieh Yu ^{1,*}, Shean-Jen Chen ¹ and YongMan Choi ^{1,*} 

¹ College of Photonics, National Yang Ming Chiao Tung University, Tainan 71150, Taiwan

² Clean Energy Conversion Research Center, Institute for Advanced Engineering, Yongin 17180, Korea

* Correspondence: cschoi@iae.re.kr (C.C.); hcyu@nycu.edu.tw (H.-C.Y.); ymchoi@nycu.edu.tw (Y.C.)

† These authors contributed equally to this work.

Abstract: Solar light-driven hydrogen by photocatalytic water splitting over a semiconductor photoelectrode has been considered a promising green energy carrier. P-type semiconducting copper oxides (Cu₂O and CuO) have attracted remarkable attention as an efficient photocathode for photoelectrochemical (PEC) water splitting because of their high solar absorptivity and optical band gaps. In this study, CuO thin films were prepared using the sol-gel spin coating method to investigate the effects of aging time and layer dependency. Electrodeposition was also applied to fabricate Cu₂O thin films. Cu₂O thin films annealed at 300 °C are a hetero-phase system composed of Cu₂O and CuO, while those at 400 °C are fully oxidized to CuO. Thin films are characterized using atomic force microscopy (AFM), scanning electron microscopy (SEM), ultraviolet-visible spectroscopy (UV-VIS), Fourier transform infrared spectroscopy (FTIR), spectroscopic ellipsometry (SE), X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and Raman microscopy. The hetero-phase thin films increase the photoconversion efficiency compared to Cu₂O. Fully oxidized thin films annealed at 400 °C exhibit a higher efficiency than the hetero-phase thin film. We also verified that CuO thin films fabricated using electrodeposition show slightly higher efficiency than the spin coating method. The highest photocurrent of 1.1 mA/cm² at 0.10 V versus RHE was measured for the fully oxidized CuO thin film under one-sun AM1.5G illumination. This study demonstrates a practical method to fabricate durable thin films with efficient optical and photocatalytic properties.

Keywords: p-type semiconductor; copper oxide; thin film; sol-gel deposition; electrodeposition; photoelectrochemical water splitting



Citation: Chang, C.-J.; Lai, C.-W.; Jiang, W.-C.; Li, Y.-S.; Choi, C.; Yu, H.-C.; Chen, S.-J.; Choi, Y. Fabrication and Characterization of P-Type Semiconducting Copper Oxide-Based Thin-Film Photoelectrodes for Solar Water Splitting. *Coatings* **2022**, *12*, 1206. <https://doi.org/10.3390/coatings12081206>

Academic Editors: Giorgos Skordaris and Fabio Palumbo

Received: 29 June 2022

Accepted: 16 August 2022

Published: 17 August 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

Hydrogen generation using solar energy through water electrolysis with solar-powered electricity and photocatalytic solar water splitting is vital to fulfill the pipe dream of the hydrogen economy, due to global demand for renewable energy [1]. Among solar energy conversion methods, photoelectrochemical (PEC) water splitting is considered one of the most pivotal and sustainable approaches to tackle the global energy crisis. It dissociates water molecules directly into hydrogen and oxygen using sunlight and semiconducting PEC materials [2]. Even if it is sustainable without producing greenhouse gases, developing novel PEC materials with excellent efficiencies, durability, and cost-effectiveness is imperative for their commercialization [3]. PEC water splitting occurs sequentially through the production of electron-hole pairs due to absorbing sunlight, the charge drift and diffusion, the separation of charge carriers, and the reduction or oxidation of water on the surfaces with the charge carriers [4]. Semiconducting PEC materials must meet several requirements to split water molecules [5]. For example, the potential of the conduction band (CB) gap

must be lower than the reaction potential of reduced water, and that of the valence band (VB) gap higher than the reaction potential of oxidized water.

The photoelectrodes for large-scale applications may be cost-effective metal oxides [6] among various semiconductor materials of metal oxides (TiO_2 and WO_3), metal sulfides (CdS and WS_2), and metal selenides (WSe_2 and ZnSe) [7]. Their ionic character originated from the hybrid orbitals of transition metal cations and oxygen ($\text{O } 2p$) could lead to a large band gap [5]. Furthermore, the VB's localized p-orbital characteristic causes the low mobility of electron holes in conventional metal oxides, resulting in no durable photoanode device producing a photocurrent greater than 10 mA/cm^2 with adequate photovoltage coupled with a photocathode [8]. In addition, metal oxides often experience short charge diffusion and slow charge transfer, owing to the formation of sluggish and self-trapped charge carriers [9]. Therefore, the search for novel, highly efficient, and cost-effective metal oxide semiconductors with a narrower band gap and a longer carrier diffusion length has attracted wide attention [10]. However, it remains a great challenge to propose high-performance materials for photocatalytic water splitting, for example, by regulating electronic band structures and creating the direct Z-scheme heterojunction (i.e., $\text{Co}_9\text{S}_8/\text{CdS}$ [11], ZnO/CdS [12], and TiO_2/CdS [13]) and the p-n heterojunction (i.e., $\text{B-C}_3\text{N}_4/\text{Mo-BiVO}_4$ [14], $\text{Cu}_2\text{O}/\text{CeO}_2$ [15], and CuO/ZnO [16]). To the best of our knowledge, no candidate material meets all requirements with a high enough energy conversion efficiency [7].

Among semiconducting photoelectrode materials, copper oxides (Cu_xO ; $x = 1$ or 2) have received remarkable attention due to their outstanding properties and numerous applications for solar-to-hydrogen conversion from water [17,18]. Copper oxides are naturally a p-type semiconductor [19] with high solar absorptivity, low thermal radiation, and low energy band gaps (Cu_2O : 2.1–2.6 eV and CuO : 1.3–2.1 eV) [20]. The band gaps also depend on sample preparation approaches and surface morphologies. Due to their high natural abundance, copper oxides can also be used for cost-effective solar cells [21]. Cu_2O -based solar cells with a band gap of 2.0 eV were reported to potentially reach a theoretical maximum efficiency of 20% [19,22] according to the Shockley-Queisser limit (SQL) [23]. Moreover, copper oxide-based photoelectrodes can be applied for photochemical CO_2 reduction [24]. Regardless of these advantages and the versatile applications of copper oxides as excellent solar absorbing materials, a grand challenge may be to rationally minimize the strong electron-hole recombination of copper oxides [22]. Various reports also address obtaining the optimal diffusion length of minority charge carriers and thicknesses of thin films [22,25]. Therefore, it may be crucial to effectively separate electron-hole pairs to improve the efficiency of photocatalytic solar water splitting using copper oxide-based photocathodes. To date, as summarized in Table S1, the fabrication of copper oxide-based photocathodes applied to PEC water splitting is a tremendous challenge that requires technological advances [26], since the efficiency (e.g., 0.10–1.75%) [17,27–37] depends on many factors, such as substrates, pH values, and surface modification. For the preparation of high-performance photoelectrode materials, metal oxide thin films can be prepared by numerous methods, including the sol-gel method, chemical vapor deposition (CVD), pulsed laser deposition (PLD), and electrodeposition. Among them, the sol-gel spin coating method is more cost-effective, faster, and higher-yield than physical methods (i.e., CVD and PLD). Its process comprises the preparation of a precursor solution, aging the solution for conversion of sol in the liquid to gel, depositing the sol-gel on a substrate by spin coating, and heat treatment of thin films. Even if the sol-gel approach is fast and straightforward compared to other thin-film deposition methods, the performance of thin films is influenced by several factors, including sol aging time and temperatures, sol concentrations, chelating agents, pre- and post-heating temperatures, and spin coating speed and time. Among the factors for preparing high-quality thin films, optimizing sol aging time and heat-treatment parameters may be essential for fabricating nanostructured thin films and controlling optical band gaps. Accordingly, this study first examined the effects of sol aging time, heat treatment, and layer dependency on p-type CuO thin films fabricated using the sol-gel spin

coating method, followed by photocatalytic solar water splitting. CuO thin films were also prepared using electrodeposition with thermal oxidation to compare with the sol-gel spin coating method. We demonstrated the effect of the substrates on photocatalytic efficiencies using indium tin oxide (ITO or tin-doped indium oxide) and fluorine-doped tin oxide (FTO) coated glass substrates since their properties are affected by thermal treatment [38,39].

2. Experimental Details

2.1. Thin-Film Preparation

The sol-gel thin-film deposition method [40] was applied on ITO (~120 nm) coated glass substrates to examine the effects of CuO sol using p-type CuO thin films. ITO substrates were sequentially cleaned in an ultrasonic bath of acetone, isopropyl alcohol (IPA), ethanol, and deionized (DI) water for 5 min, followed by drying in an oven and ozone treatment for 10 min. For spin coating, we prepared a precursor solution by adding 1 mL of ethanolamine to 15 mL of IPA under stirring, followed by mixing with 0.68 g of copper (II) acetate. After the complete dissolution of the copper acetate, a solution of 0.2 g of ethylene glycol was added. The precursor solution was stirred for 24 h in air to reach complete mixing at 1500 rpm. Impurities were removed using a 0.45 μm syringe filter [41]. Then, the sol solution was aged at room temperature for 0, 12, 24, 36, and 48 h with magnetic stirring. The prefiltered 150 μL sol solution was placed on an ITO substrate at 2000 rpm for 30 s using a spin coater in a fume hood. The spin-coated thin films were then dried at 120 $^{\circ}\text{C}$ on a hot plate for 2 min, and was pre-annealed at 350 $^{\circ}\text{C}$ for 5 min to remove precursor chemicals. All thin-film samples were subjected to a final annealing process at 400 $^{\circ}\text{C}$ on a hot plate for 2 h in air. To examine layer dependency, the pre-annealing process at 350 $^{\circ}\text{C}$ for 5 min was repeated twice, four times, six times, and eight times, followed by the final annealing process at 400 $^{\circ}\text{C}$ for 2 h. Cu₂O thin films were also fabricated on FTO (~400 nm) coated glass substrates by electrodeposition. In this study, FTO substrates were applied for electrodeposition because of their excellent chemical resistance [38]. It was performed using the chronoamperometric (CA) method at -0.36 V versus Ag/AgCl (3 M NaCl) for 20 min in a solution of 3 M lactic acid and 0.4 M CuSO₄ (pH = 9) [29] added to 40 mL of DI water. The pH value was obtained using 5 M NaOH, while the entire electrodeposition process was conducted with magnetic stirring at 100 rpm. A potentiostat (BioLogic, SP-150) was used to supply a constant current during the electrodeposition process at room temperature using a coiled platinum wire (0.5 mm diameter) as a counter electrode. To obtain hetero-phase CuO/Cu₂O and pure CuO thin films, Cu₂O thin films were thermally oxidized at 300 $^{\circ}\text{C}$ and 400 $^{\circ}\text{C}$, respectively, for 1 h in air, after cleaning the Cu₂O thin films using DI water and drying in an oven at 70 $^{\circ}\text{C}$.

2.2. Characterization of Thin-Film Samples

Atomic force microscopy (AFM, Bruker Innova, MA, USA), with the tapping mode, and scanning electron microscopy (SEM, Zeiss Auriga, Oberkochen, Germany), at an accelerating voltage of 5.0 kV and a working distance of 5.2 mm after gold coating, were employed to examine the surface morphologies of thin films. Band gaps of thin films were measured using ultraviolet-visible spectroscopy (UV-VIS, Shimadzu UV1800, Kyoto, Japan), while Fourier transform infrared spectroscopy (FTIR, Thermo Nicolet iS-10, MA, USA) was used to investigate the temperature-dependent variation of precursor chemicals. Furthermore, we characterized the optical constants using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam α -SE, Lincoln, NE, USA) to examine the thickness of CuO thin films by measuring at three different angles of 65 $^{\circ}$, 70 $^{\circ}$, and 75 $^{\circ}$. X-ray diffraction (XRD, Bruker D8 DISCOVER, Billerica, MA, USA) using Cu K $_{\alpha}$ radiation ($\lambda = 0.154184\text{ nm}$), an X-ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA) equipped with mono-chromated Al K $_{\alpha}$ radiation and a flood gun, and Raman microscopy (CL Technology UniDRON-S, New Taipei, Taiwan) with a 532 nm excitation wavelength were applied to characterize the temperature-dependent effects of thin films grown on FTO. PEC measurements were carried out with a typical three-electrode system using

Ag/AgCl (3 M NaCl) and a coiled platinum wire as reference and counter electrodes, respectively, and the working electrode of copper oxide thin films with an active area of 1.0 cm^2 in $0.2 \text{ M Na}_2\text{SO}_4$. The Nernst equation was applied to convert the potentials (V versus Ag/AgCl) to the reversible hydrogen electrode (RHE) scale (V versus RHE) [42]. The applied bias photon-to-current conversion efficiency (ABPE, %) was used to calculate the photoconversion efficiency of thin films using $\text{ABPE} = [J_P(1.23 - V_b)/P_{\text{light}}]_{\text{AM1.5G}}$, where J_P is the photocurrent density measured in mA/cm^2 , V_b is the applied bias in V, and P_{light} is the power density of incident light (AM1.5G $100 \text{ mW}/\text{cm}^2$ illumination, Enlitech SS-X, Kaohsiung, Taiwan) [43,44].

3. Results and Discussion

3.1. Sol Aging Time

The effects of the aging time of the CuO sol solution from 0 to 48 h were examined to understand the influence of structural and optical properties of CuO thin films. The AFM images of CuO thin films are displayed in Figure 1a–e. The AFM images in $3 \mu\text{m} \times 3 \mu\text{m}$ were used to quantify the root mean square (RMS) roughness of thin-film surfaces, which could be calculated from the cross-sectional profile. As illustrated in Figure 1f, the RMS roughness of CuO thin films prepared at different aging times (0, 12, 24, 36, and 48 h) corresponded to 35.5, 20.5, 15.7, 12.8, and 12.5 nm, respectively. It demonstrated that the surface of CuO thin films became smoothened by surface diffusion and were stable after 36 h. Based on the stable RMS roughness, we assumed that copper oxide grains became homogeneous after annealing because of the stable CuO sol solution. Furthermore, we measured the thickness of CuO thin films using spectroscopic ellipsometry (SE). We first verified the thickness of ITO measured using SEM ($\sim 120 \text{ nm}$) with the Cauchy model [45] used for transparent thin films. Then, the Tauc-Lorenz method was applied to examine non-transparent CuO thin films [46]. Figure 1f shows the variation of the thickness of CuO thin films by changing the aging time of the sol. It was found that the film thickness was stabilized as the surface roughness became constant after 36 h, similar to the previous study [47]. Then, we conducted absorption measurements of CuO thin films using UV-VIS spectroscopy. We observed that longer aging times (0 and 12 h) showed less absorbance, confirming that the RMS roughness was correlated with absorbance [47]. The Tauc plot analysis [48,49] with a direct transition ($\gamma = \frac{1}{2}$) resulted in the band gap of $\sim 1.99 \text{ eV}$ [20] using $(\alpha h\nu)^{1/\gamma} = B(h\nu - E_g)$, where α , h , ν , B , and E_g were the absorption coefficient, the Planck constant, the photon energy, a constant, and the energy band gap, respectively. It verified that the aging time negligibly affected the optical property of the stabilization process. Our detailed examination showed that 36 h may be imperative to fabricate stable thin films. Therefore, in this study, we used the aging time of 36 h to prepare the sol-gel CuO thin films. As summarized in Figure 2a, FTIR spectra confirmed the complete removal of precursor chemicals and the formation of metal oxide phases after 300°C . After heating as-deposited thin films, the characteristic peaks of the precursor chemical of copper(II) acetate disappeared [50], while the absorption peak at around 587 cm^{-1} assigned to the vibration of Cu(II)-O [51] appeared.

3.2. Characterization of Layer-Dependence Effects of Spin-Coated CuO Thin Films

The layer dependency of CuO thin films was performed to determine a reasonable thickness compared to that fabricated by electrodeposition. As mentioned above, the sol-gel thin-film deposition method [40] was applied on ITO substrates. As described above, two, four, six, and eight-layer CuO films were prepared. After each layer deposition, pre-annealing was conducted at 350°C for 5 min, while final thin-film samples were annealed at 400°C for 2 h. In addition to the surface morphology analysis, the band gap was obtained via the Tauc plot analysis using the absorbance spectra of each CuO thin-film layer. Figure 2b,c show the absorption spectra and averaged energy band gaps of CuO thin films with different layers. The absorption intensity increased as the thickness of the thin films became thicker, indicating that the transmittance decreased accordingly. To

improve the accuracy of the optical energy gap measurements, due to the inhomogeneity of the thin films, we measured each thin-film sample three times, resulting in 1.83, 1.73, 1.62, and 1.49 eV, respectively. The growth of grains caused a decrease in the number of grain boundaries. This led to an increase in the absorption intensity and a shift of the absorption edge to higher wavelengths. Consequently, the energy gap decreased [52]. Shown in Figure 3a–d are AFM-based images to examine the surface morphology of the layer dependency. As shown in Figure 3e, the RMS roughness analysis illustrated a linear relationship with the number of layers of CuO thin films (8.9, 15.1, 15.6, and 20.4 nm versus two, four, six, and eight layers, respectively). Furthermore, we observed that the thickness of the CuO thin film using ellipsometry with the Tauc-Lorentz method linearly increased with the growth of CuO layers (Figure 3e, 97.8, 123.9, 180.4, and 274.2 nm versus two, four, six, and eight layers, respectively). The layer-dependence study suggested that eight-layer CuO thin films under the experimental conditions were optimal for further analyses to avoid too low transmittance of CuO thin films.

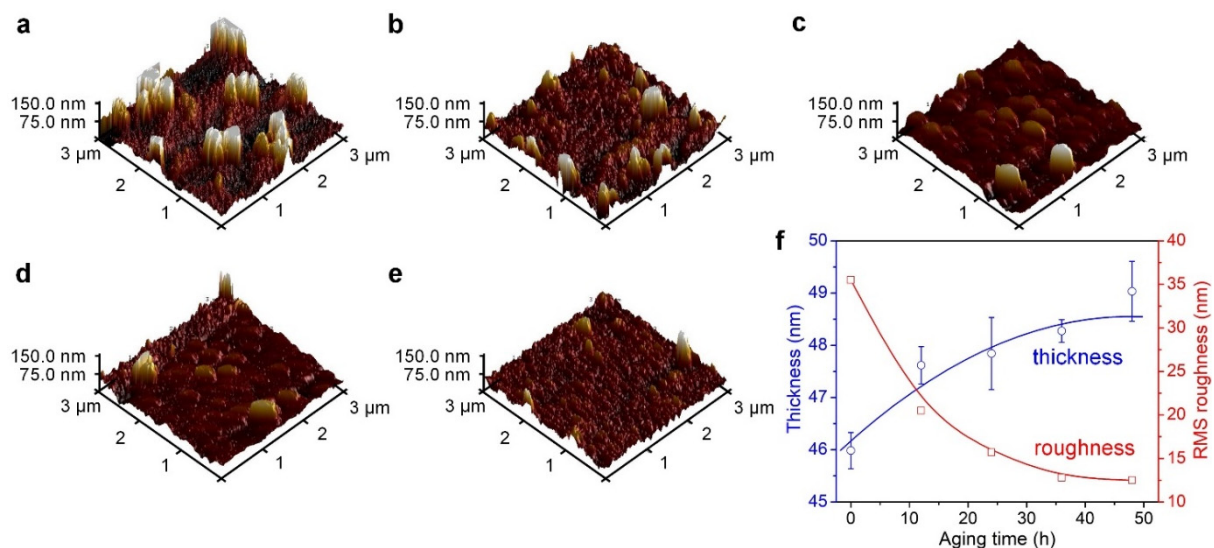


Figure 1. AFM images of CuO thin films deposited on an ITO substrate obtained with the tapping mode AFM for the aging time of (a) 0, (b) 12, (c) 24, (d) 36, and (e) 48 h. Image areas are 3 μm × 3 μm. (f) Variation of the RMS roughness as a function of aging time and the thickness of CuO thin films measured using SE.

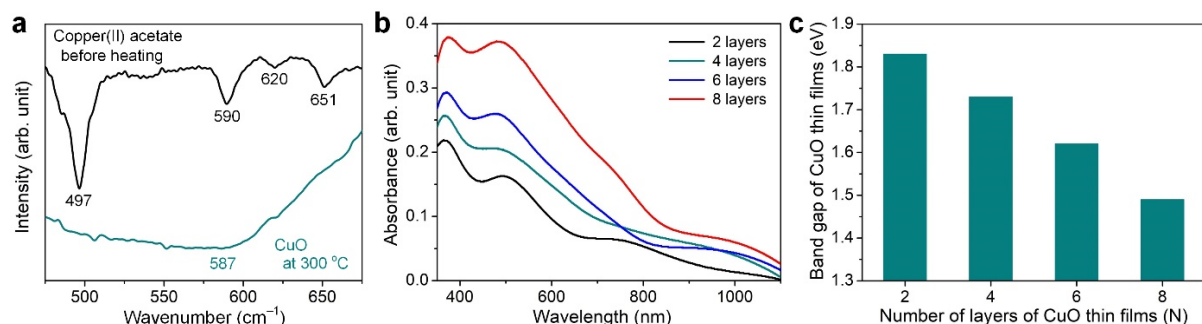


Figure 2. (a) FTIR spectra of the sol-gel spin-coated thin film before and after annealing at 300 °C in air. (b) Absorbance spectra and (c) optical band gaps with different layers of CuO thin films.

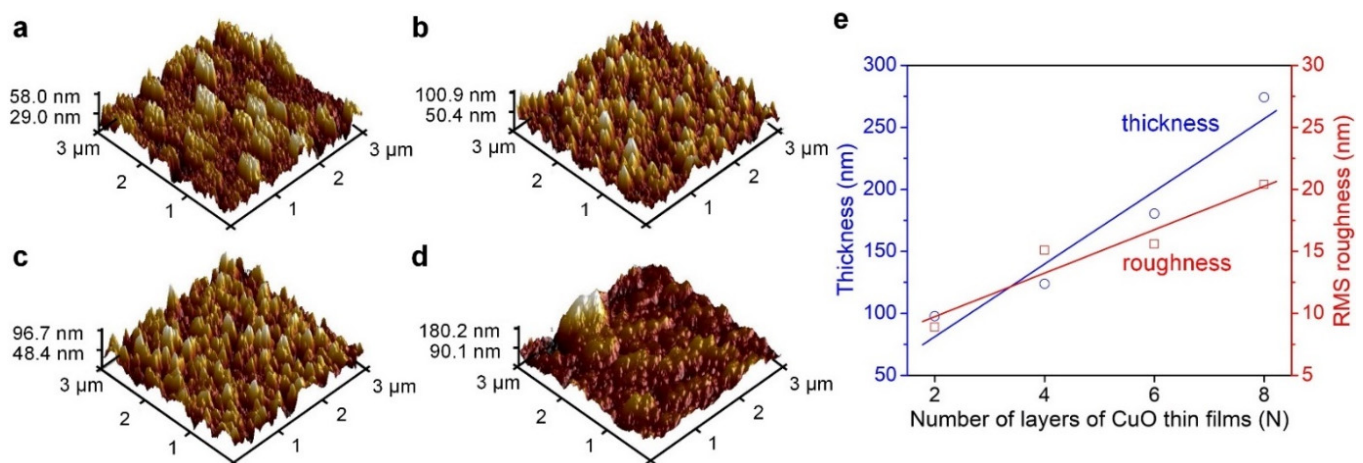


Figure 3. AFM images of (a) two, (b) four, (c) six, and (d) eight-layer CuO thin films deposited on ITO after the annealing process at 400 °C for 2 h. Image areas are 3 μm × 3 μm. (e) Variation of the RMS roughness and the thickness of CuO thin films measured using SE.

3.3. Preparation and Characterization of Copper Oxide Thin Films Using Electrodeposition

As summarized in Figure 4, we carried out SEM measurements to examine whether the surfaces of thin films, using spin coating and electrodeposition, were dense enough for PEC measurements. As an initiative, we first examined the PEC performance of CuO/ITO and CuO/FTO prepared using the sol-gel spin-coating method and annealed at 400 °C. As shown in Figure S1, the ITO-based CuO thin film showed a lower PEC performance than the FTO-based thin film, due to the change of the electrical property at >300 °C [38,39]. Accordingly, we applied the FTO substrate to examine the photoconversion efficiency in this study. We prepared yellowish-red Cu₂O thin films using electrodeposition at room temperature to fabricate hetero-phase CuO/Cu₂O and CuO films on FTO. As shown in Figure 4a,b, we observed that the thickness of electrodeposition-based thin films was approximately 100 nm. In addition, it demonstrated that the Cu₂O thin film was well prepared without cracks, and the thermally oxidized samples became denser with smaller grains. More characterizations were carried out to examine how Cu₂O was transformed into CuO after annealing. As shown in Figure 4c, the spin-coated CuO surfaces consisted of nanostructured and homogeneous grains, leading to a high surface roughness compared to Cu₂O-based samples. We assumed that these surface morphologies would influence the PEC performance because nanostructured surfaces significantly affect optical properties [53], making nanostructured photoelectrodes more effective than conventional bulk films. SEM confirmed that the thickness of the spin-coated CuO thin film on FTO was ~257 nm, which was in line with that deposited on ITO using SE (Figure 3e, ~274 nm). We conducted surface characterizations to understand the chemical composition of thin films using XRD, Raman microscopy, and XPS. As shown in Figure 5a, the two major diffraction peaks at 36.7° and 42.4° corresponding to (111) and (200) planes were attributed to Cu₂O (JCPDS file No. 05-0667) [54,55]. The spin-coated CuO (JCPDS file No. 78-0428) thin film was identified by those at 33.5°, 35.5°, and 38.6°, corresponding to (110), (002), and (111) planes [55,56]. After thermal oxidation at 300 °C, the thin film was characterized by a mixture of Cu₂O and CuO. Then, after thermal oxidation at 400 °C, the XRD patterns became identical to those of CuO, confirming the complete oxidation of Cu₂O to CuO at 400 °C under the experimental conditions. However, as the intensity of the XRD pattern was not remarkable, Raman spectroscopy was used to characterize the surfaces to complement the XRD analysis, clarifying the change of thin-film-based copper oxides. Shown in Figure 5b are Raman spectra for thin-film copper oxides deposited on FTO using spin coating and electrodeposition before and after annealing at 300 °C and 400 °C scanned in the spectral region of 100 to 800 cm⁻¹. The characteristic Raman bands for CuO at 292 cm⁻¹

and Cu_2O at 213, 529, and 633 cm^{-1} agreed with those in the literature [57]. Like the XRD measurements, we verified that the Cu_2O -based thin-film sample annealed at 400°C to become CuO , while the sample that annealed at 300°C exhibited the characteristic peaks of Cu_2O and CuO . It revealed that the Cu_2O thin films annealed at 300°C could be considered a hetero-phase system composed of CuO and Cu_2O . To identify the elemental compositions and oxidation states of CuO and Cu_2O thin-film samples prepared by the sol-gel spin coating and electrodeposition methods, XPS measurements were performed [58,59]. The survey spectra of Cu_2O and CuO deposited on FTO are shown in Figure S2, where copper and oxygen elements are characterized. The C 1s peak at 284.8 eV was applied to calibrate the XPS spectra of Cu_2O and CuO [60,61]. As shown in Figure 5c, the main peaks of the Cu_2O thin film at 932.8 eV and 952.5 eV (Cu^+) and those of the CuO thin film at 933.3 eV and 953.6 eV (Cu^{2+}) corresponded to $\text{Cu } 2p_{3/2}$ and $\text{Cu } 2p_{1/2}$, respectively [62]. Furthermore, the shake-up satellite peaks were detected in the region of 940.0–943.5 eV and at 962.2 eV [63,64]. Figure 5d shows the XPS analysis of the O 1s peaks for Cu_2O and CuO . The peak at 529.7 eV observed from the thermal oxidation sample was identified as lattice oxygen in CuO , while that at 530.3 eV was assigned to lattice oxygen in Cu_2O [65]. The optical properties of copper oxide thin films were also examined by the band gap change in the range of 300–1100 nm. All thin films exhibited higher absorption in the UV region (350 to 390 nm) than in the visible region (Figure 6a). The absorption of the Cu_2O film was greatly enhanced in the range of 400–800 nm after annealing. As shown in Figure 6b, the 2.45 eV band gap of Cu_2O aligned with those in the literature [20]. After annealing, as anticipated, its band gap shifted down to that of CuO (i.e., 1.61 eV (annealed at 300°C), 1.51 eV (annealed at 400°C), and 1.49 eV (spin-coated CuO)) [20].

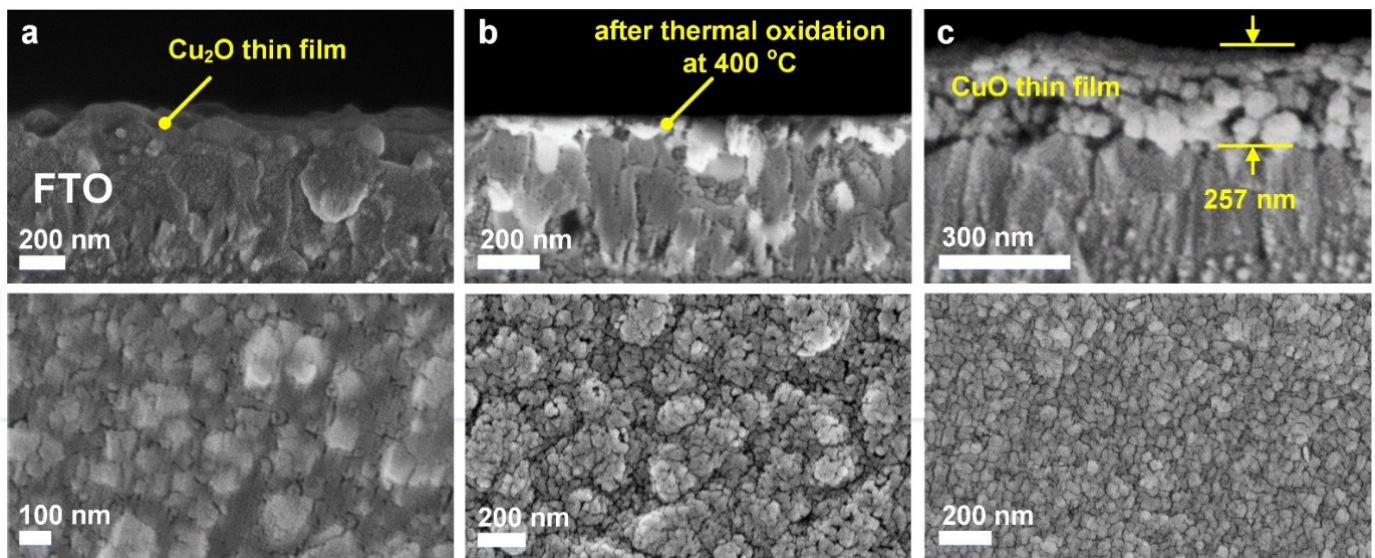


Figure 4. SEM images of cross-sectional and top views for (a) the as-prepared Cu_2O thin film by electrodeposition and (b) the thermally oxidized sample at 400°C after electrodeposition. (c) The spin-coated eight-layer CuO thin film annealed at 400°C . Thin films are deposited on FTO.

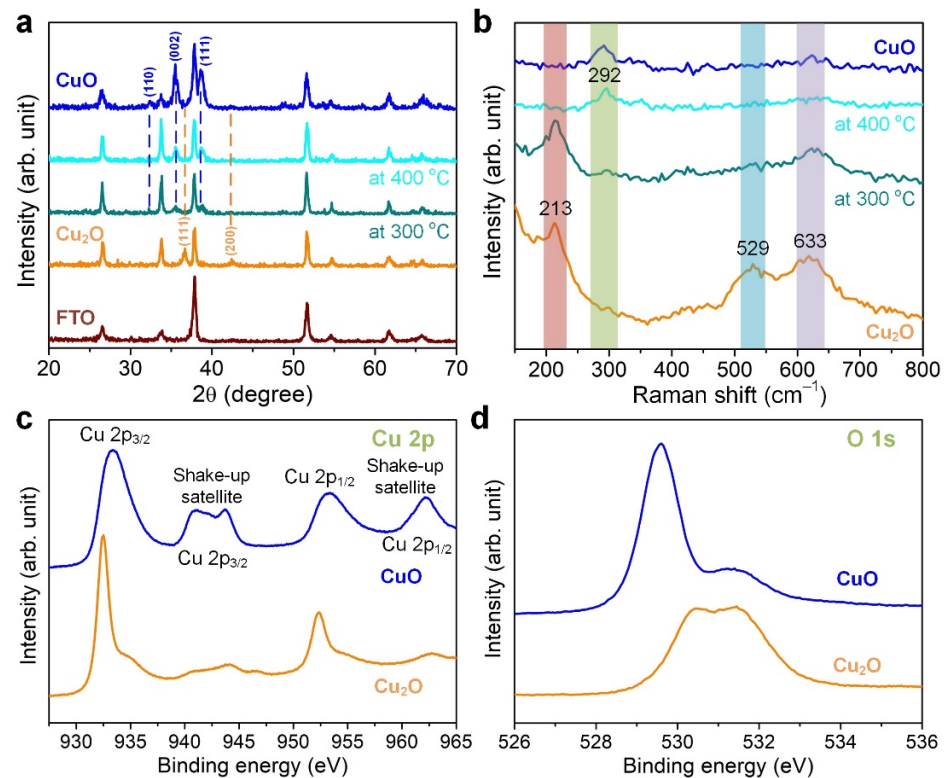


Figure 5. (a) XRD patterns and (b) Raman spectra of as-prepared Cu₂O and after thermal oxidation at 300 °C and 400 °C and CuO fabricated by the sol-gel spin coating method on FTO. XPS spectra of (c) Cu 2p and (d) O 1s for Cu₂O and CuO on FTO. The survey spectra are shown in Figure S1.

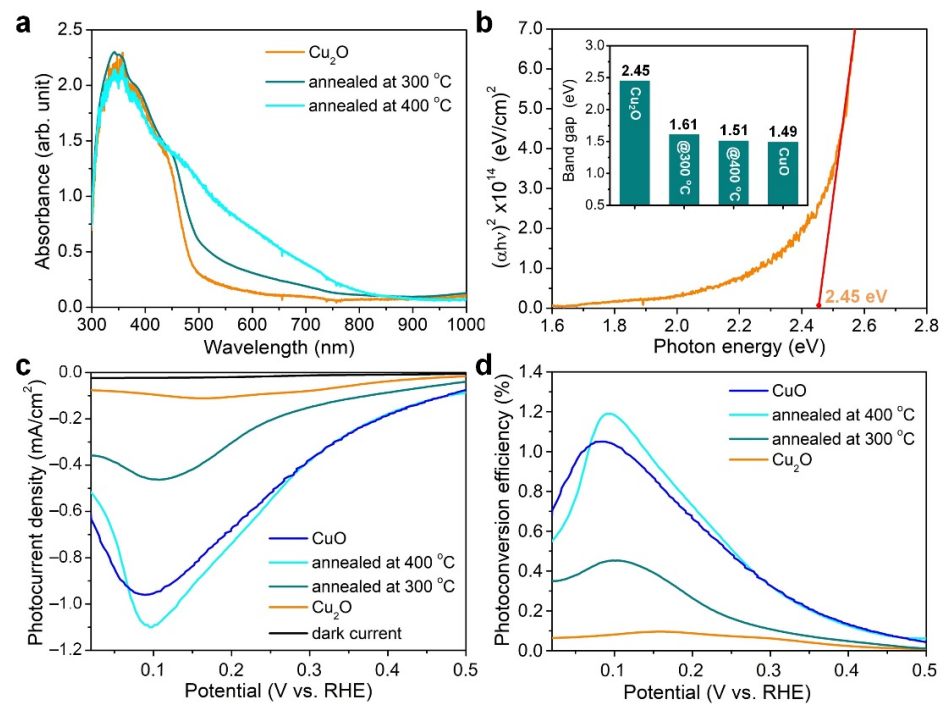


Figure 6. (a) Absorption spectra of Cu₂O and thermally oxidized at 300 °C and 400 °C, and (b) Tauc plot for the Cu₂O thin film deposited on FTO. The inset shows a comparison of the band gaps of different samples. (c) Photocurrent densities and (d) photoconversion efficiencies of Cu₂O and annealed thin films at 300 °C and 400 °C and the spin-coated CuO thin film on FTO.

3.4. Photocatalytic Solar Water Splitting Using P-Type Semiconducting Copper Oxide Thin Films

After characterizing photoelectrode materials, as summarized in Figure 6c,d, we conducted PEC water splitting experiments, demonstrating the onset potential of photoelectrodes at ~ 0.45 V [29,66]. Similar to the previous study [29], the photoconversion efficiency of Cu_2O prepared by electrodeposition was 0.09%, while thermally oxidized electrode materials at 300 °C and 400 °C showed enhanced efficiencies of 0.45% and 1.19%, respectively (Figure 6d), compared to Cu_2O . We also measured the photoconversion efficiency of the spin-coated CuO thin film, and its efficiency of 1.05% was comparable to that annealed at 400 °C. As described above, the nanostructured surface of thin films might influence the efficiency. As we characterized that Cu_2O samples annealed at 400 °C were identified as CuO , we hypothesized that electrodeposition-based electrode materials might improve photocurrent collection, owing to a better interface between the nanostructured photoelectrodes and substrates, leading to less energy loss during transport. In summary, hetero-phase thin films (Cu_2O and CuO) boosted PEC performance compared to the Cu_2O film, while a fully oxidized sample at 400 °C exhibited better performance. A rational design of high-efficiency copper oxide-based photoelectrodes might be critical to understanding the mechanisms, since the enhancement of photoconversion efficiencies through hydrogen evolution was related to the carrier concentrations of Cu_2O and CuO ($3.1 \times 10^{17} \text{ cm}^{-3}$ and $2.4 \times 10^{18} \text{ cm}^{-3}$, respectively) [29].

4. Conclusions

Cu_2O thin films were successfully fabricated using electrodeposition, while CuO thin films were also prepared using the sol-gel spin coating method. We studied the effects of aging time and layer dependency based on surface morphologies and optical property variation, suggesting an optimal eight-layer CuO thin film (~ 270 nm) for further experiments. XRD and Raman spectroscopic measurements confirmed that Cu_2O thin films annealed at 300 °C are a hetero-phase system composed of Cu_2O and CuO . It revealed that >400 °C annealing is essential for fabricating pure CuO . The surface morphology examination using SEM and AFM observed the nanostructured formation from thermal oxidation, suggesting a good junction between electrode materials and the substrate. Consequently, it may affect photoconversion efficiencies. The Tauc plot was successfully applied to measure the energy band gaps of thin films, which were consistent with those in the literature (Cu_2O : 2.45 eV and CuO : 1.49–1.51 eV). The hetero-phase thin film had a slightly larger band gap of 1.61 eV than CuO . We verified that CuO thin films fabricated via electrodeposition exhibit a slightly higher efficiency than the sol-gel spin coating method (1.19% versus 1.05%). A systematic thickness-dependent study on Cu_2O thin films, by adjusting preparation conditions (i.e., pH and temperatures of precursor solutions and annealing temperatures), may influence PEC performance by generating heterojunction layers [18,29]. This study would offer pivotal information to achieve the rational design of highly efficient and cost-effective PEC water splitting and CO_2 seawater splitting using different fabrication approaches for copper oxide-based photoelectrodes.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/coatings12081206/s1>, Table S1: Compilation of representative copper oxide-based photocathodes used for PEC water splitting, Figure S1: Comparison of photoconversion efficiencies of CuO deposited on FTO and ITO using the sol-gel spin-coating method, Figure S2: XPS survey spectrum for (a) Cu_2O and (b) CuO deposited on FTO.

Author Contributions: Conceptualization, Y.C.; data curation, C.-J.C. and C.-W.L.; investigation, C.-J.C., C.-W.L., W.-C.J. and Y.-S.L.; methodology, C.-J.C. and C.-W.L.; project administration, C.C., H.-C.Y. and Y.C.; software, C.-W.L.; supervision, Y.C.; visualization, C.-J.C. and C.-W.L.; writing—original draft preparation, C.-J.C. and C.-W.L.; writing—review and editing, C.C., H.-C.Y., S.-J.C. and Y.C. All authors have read and agreed to the published version of the manuscript.

Funding: We acknowledge the Ministry of Science and Technology of Taiwan (MOST Grant No. 110-2221-E-A49-017-MY3 and 109-2221-E-009-146). C.C. thanks the Ministry of SMEs and Startups (Project No. P0016558), Korea.

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: Not applicable.

Acknowledgments: C.-J.C. and C.-W.L. thank Cong-You Lin and Tsai-Te Wang for technical support.

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

References

- Moniz, S.J.; Shevlin, S.A.; Martin, D.J.; Guo, Z.-X.; Tang, J. Visible-light driven heterojunction photocatalysts for water splitting—A critical review. *Energy Environ. Sci.* **2015**, *8*, 731–759. [\[CrossRef\]](#)
- Montoya, J.H.; Seitz, L.C.; Chakthranont, P.; Vojvodic, A.; Jaramillo, T.F.; Nørskov, J.K. Materials for solar fuels and chemicals. *Nat. Mater.* **2017**, *16*, 70–81. [\[CrossRef\]](#) [\[PubMed\]](#)
- Dias, P.; Mendes, A. Hydrogen production from photoelectrochemical water splitting. In *Encyclopedia of Sustainability Science and Technology*; Meyers, R.A., Ed.; Springer: New York, NY, USA, 2017; pp. 1–52.
- Hisatomi, T.; Kubota, J.; Domen, K. Recent advances in semiconductors for photocatalytic and photoelectrochemical water splitting. *Chem. Soc. Rev.* **2014**, *43*, 7520–7535. [\[CrossRef\]](#) [\[PubMed\]](#)
- Yang, Y.; Niu, S.; Han, D.; Liu, T.; Wang, G.; Li, Y. Progress in developing metal oxide nanomaterials for photoelectrochemical water splitting. *Adv. Energy Mater.* **2017**, *7*, 1700555. [\[CrossRef\]](#)
- Díez-García, M.I.; Gómez, R. Progress in ternary metal oxides as photocathodes for water splitting cells: Optimization strategies. *Sol. RRL* **2022**, *6*, 2100871. [\[CrossRef\]](#)
- Saraswat, S.K.; Rodene, D.D.; Gupta, R.B. Recent advancements in semiconductor materials for photoelectrochemical water splitting for hydrogen production using visible light. *Renew. Sustain. Energ. Rev.* **2018**, *89*, 228–248. [\[CrossRef\]](#)
- Liu, C.; Dasgupta, N.P.; Yang, P. Semiconductor nanowires for artificial photosynthesis. *Chem. Mater.* **2014**, *26*, 415–422. [\[CrossRef\]](#)
- Rettie, A.J.E.; Chemelewski, W.D.; Emin, D.; Mullins, C.B. Unravelling small-polaron transport in metal oxide photoelectrodes. *J. Phys. Chem. Lett.* **2016**, *7*, 471–479. [\[CrossRef\]](#)
- Jin, H.; Guo, C.; Liu, X.; Liu, J.; Vasileff, A.; Jiao, Y.; Zheng, Y.; Qiao, S.-Z. Emerging two-dimensional nanomaterials for electrocatalysis. *Chem. Rev.* **2018**, *118*, 6337–6408. [\[CrossRef\]](#)
- Feng, C.; Chen, Z.; Jing, J.; Sun, M.; Han, J.; Fang, K.; Li, W. Synergistic effect of hierarchical structure and Z-scheme heterojunction constructed by CdS nanoparticles and nanoflower-structured Co₉S₈ with significantly enhanced photocatalytic hydrogen production performance. *J. Photochem. Photobiol.* **2021**, *409*, 113160. [\[CrossRef\]](#)
- Wang, S.; Zhu, B.; Liu, M.; Zhang, L.; Yu, J.; Zhou, M. Direct Z-scheme ZnO/CdS hierarchical photocatalyst for enhanced photocatalytic H₂-production activity. *Appl. Catal. B Environ.* **2019**, *243*, 19–26. [\[CrossRef\]](#)
- Meng, A.; Zhu, B.; Zhong, B.; Zhang, L.; Cheng, B. Direct Z-scheme TiO₂/CdS hierarchical photocatalyst for enhanced photocatalytic H₂-production activity. *Appl. Surf. Sci.* **2017**, *422*, 518–527. [\[CrossRef\]](#)
- Ye, K.-H.; Li, H.; Huang, D.; Xiao, S.; Qiu, W.; Li, M.; Hu, Y.; Mai, W.; Ji, H.; Yang, S. Enhancing photoelectrochemical water splitting by combining work function tuning and heterojunction engineering. *Nat. Commun.* **2019**, *10*, 3687. [\[CrossRef\]](#)
- Wang, Y.; Tang, G.; Wu, Y.; Zhao, J.; Zhang, H.; Zhou, M. Cu₂O/CeO₂ Photoelectrochemical water splitting: A nanocomposite with an efficient interfacial transmission path under the Co-action of p-n heterojunction and micro-mesocrystals. *Chem. Eur. J.* **2022**, *28*, e202103459.
- Zhang, K.; Cai, W.-F.; Shi, J.-W.; Chen, Q.-Y. Architecture lattice-matched cauliflower-like CuO/ZnO p-n heterojunction toward efficient water splitting. *J. Chem. Technol. Biotechnol.* **2022**, *97*, 914–923. [\[CrossRef\]](#)
- Chiang, C.-Y.; Aroh, K.; Franson, N.; Satsangi, V.R.; Dass, S.; Ehrman, S. Copper oxide nanoparticle made by flame spray pyrolysis for photoelectrochemical water splitting—Part II. Photoelectrochemical study. *Int. J. Hydrogen Energy* **2011**, *36*, 15519–15526. [\[CrossRef\]](#)
- Jeong, D.; Jo, W.; Jeong, J.; Kim, T.; Han, S.; Son, M.-K.; Jung, H. Characterization of Cu₂O/CuO heterostructure photocathode by tailoring CuO thickness for photoelectrochemical water splitting. *RSC Adv.* **2022**, *12*, 2632–2640. [\[CrossRef\]](#)
- Meyer, B.K.; Polity, A.; Reppin, D.; Becker, M.; Hering, P.; Klar, P.J.; Sander, T.; Reindl, C.; Benz, J.; Eickhoff, M.; et al. Binary copper oxide semiconductors: From materials towards devices. *Phys. Status Solidi B* **2012**, *249*, 1487–1509. [\[CrossRef\]](#)
- Murali, D.S.; Kumar, S.; Choudhary, R.J.; Wadikar, A.D.; Jain, M.K.; Subrahmanyam, A. Synthesis of Cu₂O from CuO thin films: Optical and electrical properties. *AIP Adv.* **2015**, *5*, 047143. [\[CrossRef\]](#)
- Hussain, S.; Cao, C.; Usman, Z.; Nabi, G.; Butt, F.K.; Mahmood, K.; Ali, A.; Arshad, M.I.; Amin, N. Effect of films morphology on the performance of Cu₂O PEC solar cells. *Optik* **2018**, *172*, 72–78. [\[CrossRef\]](#)
- Kunturu, P.P.; Huskens, J. Efficient solar water splitting photocathodes comprising a copper oxide heterostructure protected by a thin carbon layer. *ACS Appl. Energy Mater.* **2019**, *2*, 7850–7860. [\[CrossRef\]](#)

23. Shockley, W.; Queisser, H.J. Detailed balance limit of efficiency of p-n junction solar cells. *J. App. Phys.* **1961**, *32*, 510–519. [\[CrossRef\]](#)
24. de Brito, J.F.; Araujo, A.R.; Rajeshwar, K.; Zannoni, M.V.B. Photoelectrochemical reduction of CO₂ on Cu/Cu₂O films: Product distribution and pH effects. *Chem. Eng. J.* **2015**, *264*, 302–309. [\[CrossRef\]](#)
25. Liu, Y.; Turley, H.K.; Tumbleston, J.R.; Samulski, E.T.; Lopez, R. Minority carrier transport length of electrodeposited Cu₂O in ZnO/Cu₂O heterojunction solar cells. *Appl. Phys. Lett.* **2011**, *98*, 162105. [\[CrossRef\]](#)
26. Paracchino, A.; Mathews, N.; Hisatomi, T.; Stefik, M.; Tilley, S.D.; Grätzel, M. Ultrathin films on copper(I) oxide water splitting photocathodes: A study on performance and stability. *Energy Environ. Sci.* **2012**, *5*, 8673–8681. [\[CrossRef\]](#)
27. Xing, H.; Lei, E.; Guo, Z.; Zhao, D.; Liu, Z. Enhancement in the charge transport and photocorrosion stability of CuO photocathode: The synergistic effect of spatially separated dual-cocatalysts and p-n heterojunction. *Chem. Eng. J.* **2020**, *394*, 124907. [\[CrossRef\]](#)
28. Jian, J.; Kumar, R.; Sun, J. Cu₂O/ZnO p-n junction decorated with NiO_x as a protective layer and cocatalyst for enhanced photoelectrochemical water splitting. *ACS Appl. Energy Mater.* **2020**, *3*, 10408–10414. [\[CrossRef\]](#)
29. Yang, Y.; Xu, D.; Wu, Q.; Diao, P. Cu₂O/CuO bilayered composite as a high-efficiency photocathode for photoelectrochemical hydrogen evolution reaction. *Sci. Rep.* **2016**, *6*, 35158. [\[CrossRef\]](#)
30. Bae, H.; Burungale, V.; Na, W.; Rho, H.; Kang, S.H.; Ryu, S.-W.; Ha, J.-S. Nanostructured CuO with a thin g-C₃N₄ layer as a highly efficient photocathode for solar water splitting. *RSC Adv.* **2021**, *11*, 16083–16089. [\[CrossRef\]](#)
31. Mary, A.S.; Murugan, C.; Pandikumar, A. Uplifting the charge carrier separation and migration in Co-doped CuBi₂O₄/TiO₂ pn heterojunction photocathode for enhanced photoelectrocatalytic water splitting. *J. Colloid Interface Sci.* **2022**, *608*, 2482–2492. [\[CrossRef\]](#)
32. Baek, S.K.; Kim, J.S.; Yun, Y.D.; Kim, Y.B.; Cho, H.K. Cuprous/Cupric heterojunction photocathodes with optimal phase transition interface via preferred orientation and precise oxidation. *ACS Sustain. Chem. Eng.* **2018**, *6*, 10364–10373. [\[CrossRef\]](#)
33. Ma, M.; Lei, E.; Zhao, D.; Xin, Y.; Wu, X.; Meng, Y.; Liu, Z. The p-n heterojunction of BiVO₄/Cu₂O was decorated by plasma Ag NPs for efficient photoelectrochemical degradation of Rhodamine B. *Colloids Surf. A Physicochem. Eng. Asp.* **2022**, *633*, 127834. [\[CrossRef\]](#)
34. Hossain, R.; Nekouei, R.K.; Al Mahmood, A.; Sahajwalla, V. Value-added fabrication of NiO-doped CuO nanoflakes from waste flexible printed circuit board for advanced photocatalytic application. *Sci. Rep.* **2022**, *12*, 12171. [\[CrossRef\]](#) [\[PubMed\]](#)
35. Chen, Y.-C.; Dong, P.-H.; Hsu, Y.-K. Defective indium tin oxide forms an ohmic back contact to an n-type Cu₂O photoanode to accelerate charge-transfer kinetics for enhanced low-bias photoelectrochemical water splitting. *ACS Appl. Mater. Interfaces* **2021**, *13*, 38375–38383. [\[CrossRef\]](#)
36. Zhong, X.; Song, Y.; Cui, A.; Mu, X.; Li, L.; Han, L.; Shan, G.; Liu, H. Adenine-functionalized graphene oxide as a charge transfer layer to enhance activity and stability of Cu₂O photocathode for CO₂ reduction reaction. *Appl. Surf. Sci.* **2022**, *591*, 153197. [\[CrossRef\]](#)
37. Kalanur, S.S.; Lee, Y.J.; Seo, H. Enhanced and stable photoelectrochemical H₂ production using an engineered nano multijunction with Cu₂O photocathode. *Mater. Today Chem.* **2022**, *26*, 101031. [\[CrossRef\]](#)
38. Zardetto, V.; Brown, T.M.; Reale, A.; Di Carlo, A. Substrates for flexible electronics: A practical investigation on the electrical, film flexibility, optical, temperature, and solvent resistance properties. *J. Polym. Sci. B Polym. Phys.* **2011**, *49*, 638–648. [\[CrossRef\]](#)
39. Li, F.; Chen, C.; Tan, F.; Li, C.; Yue, G.; Shen, L.; Zhang, W. Semitransparent inverted polymer solar cells employing a sol-gel-derived TiO₂ electron-selective layer on FTO and MoO₃/Ag/MoO₃ transparent electrode. *Nanoscale Res. Lett.* **2014**, *9*, 579. [\[CrossRef\]](#)
40. Oral, A.Y.; Menşur, E.; Aslan, M.H.; Başaran, E. The preparation of copper(II) oxide thin films and the study of their microstructures and optical properties. *Mater. Chem. Phys.* **2004**, *83*, 140–144. [\[CrossRef\]](#)
41. Lim, Y.-F.; Chua, C.S.; Lee, C.J.J.; Chi, D. Sol-gel deposited Cu₂O and CuO thin films for photocatalytic water splitting. *Phys. Chem. Chem. Phys.* **2014**, *16*, 25928–25934. [\[CrossRef\]](#)
42. Wang, L.; Lee, C.-Y.; Schmuki, P. Solar water splitting: Preserving the beneficial small feature size in porous α -Fe₂O₃ photoelectrodes during annealing. *J. Mater. Chem. A* **2013**, *1*, 212–215. [\[CrossRef\]](#)
43. Chu, S.; Li, W.; Yan, Y.; Hamann, T.; Shih, I.; Wang, D.; Mi, Z. Roadmap on solar water splitting: Current status and future prospects. *Nano Futures* **2017**, *1*, 022001. [\[CrossRef\]](#)
44. Masoumi, Z.; Tayebi, M.; Lee, B.-K. Ultrasonication-assisted liquid-phase exfoliation enhances photoelectrochemical performance in α -Fe₂O₃/MoS₂ photoanode. *Ultrason. Sonochem.* **2021**, *72*, 105403. [\[CrossRef\]](#) [\[PubMed\]](#)
45. Elmas, S.; Korkmaz, Ş.; Pat, S. Optical characterization of deposited ITO thin films on glass and PET substrates. *Appl. Surf. Sci.* **2013**, *276*, 641–645. [\[CrossRef\]](#)
46. Trzcinski, M.; Antończak, A.; Domanowski, P.; Kustrá, M.; Wachowiak, W.; Naparty, M.; Hiller, T.; Bukaluk, A.; Wronkowska, A. Characterisation of coloured TiO_x/Ti/glass systems. *Appl. Surf. Sci.* **2014**, *322*, 209–214.
47. Li, Y.M.; Xu, L.-h.; Li, X.; Shen, X.Q.; Wang, A. Effect of aging time of ZnO sol on the structural and optical properties of ZnO thin films prepared by so-gel method. *Appl. Surf. Sci.* **2010**, *256*, 4543–4547. [\[CrossRef\]](#)
48. Jacob, S.S.K.; Kulandaisamy, I.; Raj, I.L.P.; Abdeltawab, A.A.; Mohammady, S.Z.; Ubaidullah, M. Improved optoelectronic properties of spray pyrolysis coated Zn doped Cu₂O thin films for photodetector applications. *Opt. Mater.* **2021**, *116*, 111086. [\[CrossRef\]](#)

49. Tauc, J.; Grigorovici, R.; Vancu, A. Optical properties and electronic structure of amorphous germanium. *Phys. Status Solidi B* **1966**, *15*, 627–637. [[CrossRef](#)]
50. Singhal, A.; Pai, M.R.; Rao, R.; Pillai, K.T.; Lieberwirth, I.; Tyagi, A.K. Copper(I) oxide nanocrystals—One step synthesis, characterization, formation mechanism, and photocatalytic properties. *Eur. J. Inorg. Chem.* **2013**, *2013*, 2640–2651. [[CrossRef](#)]
51. Zhang, Y.C.; Tang, J.Y.; Wang, G.L.; Zhang, M.; Hu, X.Y. Facile synthesis of submicron Cu₂O and CuO crystallites from a solid metallorganic molecular precursor. *J. Cryst. Growth* **2006**, *294*, 278–282. [[CrossRef](#)]
52. Li, J.; Kolekar, S.; Ghorbani-Asl, M.; Lehnert, T.; Biskupek, J.; Kaiser, U.; Krashennnikov, A.V.; Batzill, M. Layer-dependent band gaps of platinum dichalcogenides. *ACS Nano* **2021**, *15*, 13249–13259. [[CrossRef](#)]
53. Al-Enizi, A.M.; Shaikh, S.F.; Tamboli, A.M.; Marium, A.; Ijaz, M.F.; Ubaidullah, M.; Moydeen Abdulhameed, M.; Ekar, S.U. Hybrid ZnO flowers-rods nanostructure for improved photodetection compared to standalone flowers and rods. *Coatings* **2021**, *11*, 1464. [[CrossRef](#)]
54. Prabu, R.D.; Valanarasu, S.; Ganesh, V.; Shkir, M.; Kathalingam, A.; AlFaify, S. Effect of spray pressure on optical, electrical and solar cell efficiency of novel Cu₂O thin films. *Surf. Coat. Technol.* **2018**, *347*, 164–172. [[CrossRef](#)]
55. Panzeri, G.; Cristina, M.; Jagadeesh, M.S.; Bussetti, G.; Magagnin, L. Modification of large area Cu₂O/CuO photocathode with CuS non-noble catalyst for improved photocurrent and stability. *Sci. Rep.* **2020**, *10*, 18730. [[CrossRef](#)]
56. Moumen, A.; Hartiti, B.; Comini, E.; El Khalidi, Z.; Arachchige, H.M.M.M.; Fadili, S.; Thevenin, P. Preparation and characterization of nanostructured CuO thin films using spray pyrolysis technique. *Superlattices Microstruct.* **2019**, *127*, 2–10. [[CrossRef](#)]
57. Balik, M.; Bulut, V.; Erdogan, I.Y. Optical, structural and phase transition properties of Cu₂O, CuO and Cu₂O/CuO: Their photoelectrochemical sensor applications. *Int. J. Hydrogen Energy* **2019**, *44*, 18744–18755. [[CrossRef](#)]
58. Ghodselahe, T.; Vesaghi, M.; Shafiekhani, A.; Baghizadeh, A.; Lameii, M. XPS study of the Cu@Cu₂O core-shell nanoparticles. *Appl. Surf. Sci.* **2008**, *255*, 2730–2734. [[CrossRef](#)]
59. Poulston, S.; Parlett, P.; Stone, P.; Bowker, M. Surface oxidation and reduction of CuO and Cu₂O studied using XPS and XAES. *Surf. Interface Anal.* **1996**, *24*, 811–820. [[CrossRef](#)]
60. Li, J.P.H.; Zhou, X.; Pang, Y.; Zhu, L.; Vovk, E.I.; Cong, L.; van Bavel, A.P.; Li, S.; Yang, Y. Understanding of binding energy calibration in XPS of lanthanum oxide by in situ treatment. *Phys. Chem. Chem. Phys.* **2019**, *21*, 22351–22358. [[CrossRef](#)]
61. Greczynski, G.; Hultman, L. Compromising science by ignorant instrument calibration—Need to revisit half a century of published XPS data. *Angew. Chem. Int. Ed.* **2020**, *59*, 5002–5006. [[CrossRef](#)]
62. Hiraba, H.; Koizumi, H.; Kodaira, A.; Nogawa, H.; Yoneyama, T.; Matsumura, H. Influence of oxidation of copper on shear bond strength to an acrylic resin using an organic sulfur compound. *Materials* **2020**, *13*, 2092. [[CrossRef](#)]
63. Svintsitskiy, D.A.; Kardash, T.Y.; Stonkus, O.A.; Slavinskaya, E.M.; Stadnichenko, A.I.; Koscheev, S.V.; Chupakhin, A.P.; Boronin, A.I. In Situ XRD, XPS, TEM, and TPR study of highly active in CO oxidation CuO nanopowders. *J. Phys. Chem. C* **2013**, *117*, 14588–14599. [[CrossRef](#)]
64. Dubale, A.A.; Pan, C.-J.; Tamirat, A.G.; Chen, H.-M.; Su, W.-N.; Chen, C.-H.; Rick, J.; Ayele, D.W.; Aragaw, B.A.; Lee, J.-F.; et al. Heterostructured Cu₂O/CuO decorated with nickel as a highly efficient photocathode for photoelectrochemical water reduction. *J. Mater. Chem. A* **2015**, *3*, 12482–12499. [[CrossRef](#)]
65. Martin, L.; Martinez, H.; Poinot, D.; Pecquenard, B.; Le Cras, F. Comprehensive X-ray photoelectron spectroscopy study of the conversion reaction mechanism of CuO in lithiated thin film electrodes. *J. Phys. Chem. C* **2013**, *117*, 4421–4430. [[CrossRef](#)]
66. Kyesmen, P.I.; Nombona, N.; Diale, M. A Promising three-step heat treatment process for preparing CuO films for photocatalytic hydrogen evolution from water. *ACS Omega* **2021**, *6*, 33398–33408. [[CrossRef](#)]