Different Annealing Atmosphere Gases on the Growth and Photocurrent Performance of CuO Films Grown on FTO Substrate

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ABSTRACT: Improvement in photocurrent performance remains the key subject to prepare a stable and efficient photocathode in photoelectrochemical cell (PEC) water splitting. Different to the ordinary methods, various annealing atmosphere gases were used to study the growth of CuO films on fluorine-doped tin oxide substrate; then, the photocurrent performance was studied when those CuO films were used as photocathodes in PEC. The scanning electron microscopy images indicate that all of the CuO films are composed of vertically arrayed CuO nanosheets, each individual nanosheet with a thickness of 100–500 nm. Those hierarchical CuO photoelectrodes in the PEC exhibit quite different photoelectrochemical activities in visible light, where the air-annealed CuO film has nearly 6 times enhancement in photocurrent (108 μA) at 0 V compared to that of film under oxygen atmosphere, and 34 times of argon. It has an acceptor concentration of 2.9 × 10^{21} cm^{-3} from Mott–Schottky analysis, which is more than 2 times larger than that of the oxygen-annealed CuO film, and 37 times larger than that of the argon-annealed ultraviolet photoelectron spectroscopy measurements were carried out to explain the improved photocurrent performance of the air-annealed CuO films, where the obtained valence band of 0.44 eV and work function of 4.92 eV well match the reduction reaction of electrolyte (H_{2}O).

INTRODUCTION

To obtain high photocurrent performance in photoelectrochemical cell (PEC) water splitting, copper oxides, such as cupric oxide (CuO) and cuprous oxide (Cu_{2}O), have attracted great attentions due to their low cost, facile fabrication process, and fast time response when they are used as photodetectors and photovoltaic devices. Both the cuprous oxide (Cu_{2}O) with a band gap energy of ∼2.1 eV and the cupric oxide with a band gap energy of ∼1.5 eV have a strong absorption for solar light and are an ideal photocatalytic electrode material.

For the PEC water splitting cell, under light illumination, the electrode material will absorb light and, at the same time, the separation of the electron–hole pairs happens, where the electrons from the conduction band of CuO will reduce the hydroxyl radicals (OH^{+}) to OH^{-} anions (e^{-} + OH^{+} → OH^{-}) at the CuO/electrolyte interface and the holes move from the CuO valence band through the fluorine-doped tin oxide (FTO) into the external circuit to the Pt layer. Different methods have been used to improve the photocathode’s performance. For example, the enhanced photocurrent of the CuO photocathode was realized by tuning the crystallinity and surface morphology of films by rapid thermal treatment by Masudy-Panah et al. Meanwhile, the porous structure was reported to result in an efficient photocathodic reaction under UV and visible light illumination. And the photocathode with the hierarchical structure produced an unprecedentedly high photocurrent density. The mixed-phase Cu_{x}/CuO poly-crystalline NRs showed improved photocatalytic properties.

It is a common and effective method to improve charge transport by controlling the atomic vacancies in a semiconductor in a photoelectrochemical environment, and the vacancy created by oxygen (copper excess or oxygen deficient) was widely used to realize better p-type conducting properties of CuO. The common method to vary the vacancies was varying annealing temperature, which will influence on the materials’ crystallinity, optical absorption, and grain size. But using different types of gases to change the vacancies of CuO was rarely reported.

The good conductivity and the high specific surface area are requisite for high photocurrent performance in PEC, as the former provides fast carrier transport and the latter ensures enough light absorption. Therefore, in this paper, self-assembly CuO nanosheet arrays grown on a FTO substrate were prepared via a template-free growth method using copper(II) nitrate trihydrate and ammonium hydroxide as precursors and subsequently the prepared films were oxidized in a quartz tube furnace at a temperature of 200 °C for 60 min under conditions of air, oxygen (O_{2}), and argon (Ar) flow atmosphere. Finally, the annealed CuO nanoplates were used...
as photocathode to study the photocurrent performance at the annealing conditions in the PEC.

The results showed that the air-annealed CuO film demonstrates a great enhancement in photocurrent compared to that of Ar- and oxygen-annealed films. And the mechanism behind was discussed.

■ EXPERIMENTAL SECTION

All chemicals used in this study had analytical-grade purity. Copper(II) nitrate trihydrate and ammonium hydroxide were purchased from Sinopharm Chemical Reagent Co., Ltd. Fluorine-doped tin oxide (FTO) slides (7–8 Ω resistance) were provided by Hefei Kejing Materials Technology Co., Ltd. Self-assembly CuO nanosheet arrays grown on an FTO substrate were prepared via a template-free growth method using copper(II) nitrate trihydrate and ammonium hydroxide as precursors. A growth solution prepared by dissolving 1.165 g of Cu(NO_{3})_{2}·3H_{2}O was dissolved in 40 mL of deionized water under constant magnetic stirring for approximately 10 min. Then, 2 mL of ammonium hydroxide (25 wt %) was added dropwise to the green aqueous solution. The solution was then kept at 70 °C without stirring in a drying oven. A piece of FTO substrate (1 cm × 1 cm), which had been ultrasonically cleaned in acetone and subsequently in deionized water, was then hung in the growth solution for various reaction times at 70 °C and then a large-area uniform light-blue film covering the FTO substrate surface was observed. The resulting films were rinsed with deionized water and subsequently dried in air at approximately 60 °C. It should be mentioned that almost all precursor films strongly adhere to the FTO substrate and cannot be removed from the substrate by ultrasonic vibration in water. Here, three precursor films were obtained with reaction times of 60, 180, and 240 min and then were oxidized in a quartz tube furnace at 200 °C for 60 min under air, oxygen (O_{2}), and argon (Ar) flow, respectively, corresponding to samples #air (#3 h), #O_{2}, and #Ar. After heat treatment, dark films under the FTO substrates were finally achieved.

■ CHARACTERIZATION

The prepared samples were characterized by X-ray diffraction (XRD) with Cu Kα radiation (λ = 0.154 nm), scanning electron microscopy (SEM) using a Hitachi S-4800 microscope, transmission electron microscopy (TEM), and high-resolution transmission electron microscopy (HRTEM) using a Tecnai G2 F30 operated at an accelerating voltage of 300 kV. Absorption spectra were carried out by using a Varian Cary 50 UV−visible spectrophotometer. And X-ray photoelectron spectroscopy (XPS) and ultraviolet photoelectron spectroscopy (UPS) measurements were conducted on an ESCALAB-250Xi photoelectron spectroscope.

■ PEC MEASUREMENTS

PEC measurements were conducted in a typical three-electrode electrochemical cell controlled by a Zanner CIMPS electrochemical workstation (Germany) in 0.2 M Na_{2}SO_{4}, where the Pt wire was used as the counter electrode, Ag/AgCl in saturated KCl as the reference electrode, and the prepared CuO nanosheet arrays with an area of 1 × 1 cm² were used as the working electrode. Visible light with a wavelength of 564 ± 60 nm was used as the illumination source with a maximum output power of 120 mW/cm².

■ RESULTS AND DISCUSSION

Morphology and Structure. To clearly see the effect of reaction time on growth process in the above-mentioned method, we present the SEM images of precursor films grown on FTO substrates with various reaction times in Figure 1a−c. SEM observation shows that the as-prepared precursor films covering the FTO substrate are mainly composed of compact stacked nanoplates with uniform size and distribution on the
As shown in Figure 1a, a reaction time of 120 min leads to a large amount of nanoplates randomly stacked compact together to form a nanoplate network. In the high-magnified SEM image (inset in Figure 1a), the nanoplates were estimated to be ∼300 nm in thickness and ∼1 μm in width. Further increasing the reaction time to 180 min, the precursor film was composed of clustered nanoplates (Figure 1b). A magnified SEM image indicates that these nanoplates were ∼100 nm in thickness and 2 μm in edge length, as clearly shown in the inset of Figure 1b. It should be noted that this type of spontaneous nanoplates have unique low-dimensional nanostructures with high specific surface areas, which may be particularly beneficial for photoelectrochemical applications as the large specific surface area and ultrathin nanoplates play critical roles in electron–hole separation.

After 240 min reaction time, as shown in Figure 1c, these well-ordered nanoplates are vertically grown on the FTO substrate and the nanoplates become thicker, with an average thickness of ∼600 nm and width of 5 μm. Additionally, the fracture cross section of precursor film obtained at 120 min was evaluated after cutting with a roll glass cutter. An FTO layer of ∼1.5 μm thickness was observed on a glass substrate (Figure 1d). The precursor film self-assembled with nanoplates with a thickness of ∼5 μm vertically grew on the FTO layer to form a dense network structure. Under different annealing gases of oxygen and argon flow at a temperature of 200 °C for 60 min, the SEM images are displayed in Figure 1e,f. After annealing treatment, a similar morphology was observed for samples #O2 and #Ar, but sample #O2 has sparse nanoplates and more voids (Figure 1e), and sample #Ar has thicker nanoplates with a thickness of 500 nm (Figure 1f). The difference in the thickness needs to be further studied.

To characterize the crystalline structure of the produced films, the XRD patterns of three as-synthesized films under air-annealing were recorded (Figure 2a,b). The XRD patterns presented in Figure 2a indicate the crystalline structure evolution of the unannealed precursor films grown on an FTO substrate with various reaction times: 120, 180, and 240 min. Generally, the diffraction peaks of all of the precursor films in Figure 2a can be indexed as an orthorhombic phase Cu(OH)$_2$ according to JCPDS card no. 13-0420, along with a marked asterisk of the FTO substrate.
plane at around $2\theta = 34.1^\circ$ is dominated by other diffraction planes. The relatively high intensity of the latter designates a strong preferential orientation of the [002] axis vertical to the FTO substrate. On further increasing the reaction time to 240 min, narrowing and enhancing intense of prominent peak at $2\theta = 34.1^\circ$ was clearly observed, indicating that longer reaction time helps adatoms to reach the favorite lattice position more easily and induces [002] orientation. This evolution of structures is consistent with the SEM observation of well-ordered nanoplates locally in parallel. In addition, the inset in Figure 2a shows light-blue Cu(OH)$_2$ ordered nanoplates locally in parallel. In addition, the inset in Figure 2b. TEM images of the single as-synthesized nanoplate and that carried out as shown in Figure 3c,d. For Cu 2p, the typical peaks were observed at 933.4 and 953.4 eV for three samples, which correspond to Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ peaks of Cu$^{2+}$, respectively. For O 1s, the peak at 530 eV can be deconvoluted into three peaks O$_1$, O$_2$, and O$_3$, as shown in Figure 3e,f. The O 1s spectra exhibit three strong peaks, labeled as “O1”, “O2”, and “O3”, with respective binding energies equal to $\sim$529.6, 531.2, and 532.4 eV, as shown in Table 1. Peaks O1 and O2 were ascribed to the O$^{2-}$ ions of the crystalline network (Cu–O) and subsurface O$^{2-}$ species, respectively. And peak O2 was also ascribed to the localized oxygen at the sites of nanoparticles’ contact in the interunit space. The higher peak (O3) is regarded as oxygen atoms chemisorbed/adsorbed at the surface. The fitting shows that the ratio of O$^{2-}$ ions (O1) of the crystalline...
network (Cu–O) to the total integrated intensity of sample #air is the highest, the lowest is for the sample #Ar; peak O2 of sample #Ar is the largest; and the oxygen atoms chemisorbed/adsorbed at the surface for sample #O2 is the largest. More localized oxygen at the nanoparticles’ contact sites will result in a trapping center, which will lower the carrier concentration.

PEC Properties. The measurement of the self-powered PEC-type detector was carried out by using Ag/AgCl as a reference electrode in saturated KCl, Pt wire as a counter electrode, and CuO films grown on the FTO substrate as an active photocathode, as shown in Scheme 1. Here, the incident light source was an LED irradiation using continuous visible light (564 ± 60 nm) pulse with an on–off interval of 20 s at different intensities.

Table 1. O 1s Spectra for Samples #Air, #O2, and #Ar

| sample | no. | peaks (nm) | ratio (%) |
|--------|-----|------------|-----------|
| #air   | O1  | 529.6      | 56.2      |
|        | O2  | 531.2      | 26.2      |
|        | O3  | 532.5      | 17.6      |
| #O2    | O1  | 529.6      | 49.2      |
|        | O2  | 531.2      | 32.7      |
|        | O3  | 532.1      | 18.7      |
| #Ar    | O1  | 529.7      | 46.8      |
|        | O2  | 531.4      | 39.2      |
|        | O3  | 532.8      | 13.7      |

Scheme 1. Schematic Device Structure of the CuO Nanoplates PEC-Type Detector

Samples #2, #3, and #4 h were used as the active photocathode in PEC under on/off of 20 s at 0.0 V vs Ag/AgCl with illumination of 564 ± 60 nm 120 mW/cm² incident intensity, and the maximal photocurrent observed was ~120 μA for sample #3 (or sample #air), as shown in Figure 4a. The photocurrent can keep up to 80% after 10 repeat cycles under on/off switching irradiation, and the maximal photosensitivity (a ratio of photocurrent to dark current) is about 22 for sample #3 (Figure 4a), meaning that the photodetector has an excellent reproducible and high photosensitive performance. After 10 circles, sample #3 has the photocurrent of 96 μA, which is nearly 25% larger than the value of 77 μA for samples #2 and #4.

To study the effects of calcining atmosphere on the photocurrent, samples #air, #O2, and #Ar were used as the active photocathode in PEC under same conditions, and their corresponding photocurrents are obtained as 120, 17.5, and 3.5 μA, as shown in Figure 4b. It shows that sample #air has nearly 7 times enhancement in photocurrent compared to sample #O2 and 34 times enhancement compared to sample #Ar. Therefore, the calcining atmosphere has a great influence on the photocurrent of CuO thin films. Figure 4c displays the transient decay times. Figure 4d shows the logarithmic plots of the photocurrent transient decay D of samples #air and #O2 without applied biases with the relation $D = (I_s - I_t)/(I_{m} - I_t)$, where $I_s$ is the current at time $t$, $I_t$ is the stabilized current, and $I_{m}$ is the current spike. Then, the transient decay time $\tau$, defined as the time at which $D = -1$, is obtained as 10.2 s for sample #air, while for sample #O2, the transient decay time $\tau$ is hard to be extracted. The longer $\tau$ means an enhanced charge separation efficiency and prolonged carrier lifetimes. The relationship between photocurrent ($I$) and incident intensity ($P$) for sample #air was plotted, as shown in Figure 4ef. A value of $\theta = 0.59$ was extracted from the relation $I \propto P^\theta$. Nonlinear power $\theta$ was regarded as the existence of the carrier traps on the CuO surface, and the result is quite smaller than the $\theta$ (~1) reported by Hong et al. A typical overshoot (spiked cathodic pulses) in the photocurrent response with time was observed obviously in Figure 4, which was explained as electron/hole recombination mediated by the trap. As discussed in ref 21, an excited electron from the conduction band will recombine with a hole from the valence band at a trap state, inducing trap-assisted recombination. In our study, we found that the electrochemical specific surface area of sample #air is larger than that of samples #Ar and #O2, as shown in Figure 5. This result demonstrates that the improved photocurrent can be ascribed to the increased specific surface.

Mechanism. Mott–Schottky (MS) plots were obtained from the electrochemical impedance spectroscopy measurement for samples #air, #O2, and #Ar, as shown in Figure 6a,b. From MS curves, the capacitance of the space charge region, formed at the semiconductor/electrolyte interface, is measured to determine the active concentration of dopants. The MS equation is described by

$$\frac{1}{C^2} = \frac{2}{N_A e \varepsilon_0} \left( \frac{V - V_{FB}}{kT} - \frac{1}{e} \right)$$

where $k$, $N_A$, $C$, and $e$ are the Boltzmann constant, hole carrier density, space charge capacitance in the semiconductor, and elemental charge value, respectively. Parameters $\varepsilon$ and $\varepsilon_0$ are the relative permittivity of the semiconductor ($\varepsilon$ of CuO is 10.26) and the permittivity of vacuum, respectively. $V$ and $T$ are the applied potential and temperature, respectively. The slope of the linear part of the curve in the Mott–Schottky plot is negative from ~0.2 to 0 V (Figure 6b), indicating a p-type semiconductor, and the hole carrier density $N_A$ can be calculated from the following relation:

$$N_A = \frac{2}{\varepsilon e \varepsilon_0 \times \text{slope}}$$

and then the acceptor concentrations are estimated as $2.9 \times 10^{21}$, $1.17 \times 10^{21}$, and $7.75 \times 10^{20}$ cm$^{-3}$ for samples #air, #O2, and #Ar, respectively. The $N_A$ value of sample #air is more than 2 times larger than that of sample #O2, and 37 times larger than that of sample #Ar. The changes in the acceptor concentrations for three samples are consistent with their photocurrent values, that is, the larger $N_A$ the better photocurrent performance will be. While our result is different from the one reported by Mallows et al., who showed that the higher oxygen pressure effectively increased the amount of nickel vacancies, leading to 1 order enhancement in acceptor concentrations.

UPS measurements were carried out to study the surface electron behavior, as shown in Figure 6c,d, where Figure 6c is a view of the secondary electron edge (SEE) energy corresponding to the left spectra in UPS data, and Figure 6d is a view of...
the valence band maximum (VBM) region corresponding to the right spectra in UPS data. The work function can be extracted from the left-hand side of the SEE spectra, which is equal to \( \sim 4.92 \) eV for samples \#air and \#O\(_2\), and 4.92 and 5.22 eV for sample \#Ar, the former is corresponding to the inner parts of CuO film and the latter to the surface. And the valence band maximum energy can be obtained from Figure 6d, which is \( \sim 0.44 \) eV for sample \#air and 0.55 eV for samples \#O\(_2\) and \#Ar. Then, the conduction band and valence band (vs vacuum) can be obtained, as shown in Table 2. For example, the conduction band is equal to 4.05 eV and the valence band is equal to 5.36 eV (vs vacuum) for sample \#air. As the minimal conduction band energy of 4.05 eV (vs vacuum energy) is more positive than the redox potential of \( \text{H}_2\text{O}/\text{H}_2 \) (4.44 V), photogenerated electrons cannot be transferred to reduce water to hydrogen; furthermore, the inner part has only fewer CuO nanoparticles to contact with electrolyte (\( \text{H}_2\text{O} \)), resulting in a decrease in the photocurrent performance. Therefore, the photocurrent of \#Ar is much lower than that of \#air.

When the CuO layer was deposited on the FTO substrate, a depletion region formed on both the FTO and CuO sides by carrier diffusion under thermal equilibrium conditions, leading to the formation of a built-in electric field near the CuO/FTO interface. At the CuO/electrolyte interface, p-type semiconductor CuO with a carrier density of \( \sim 2.9 \times 10^{21} \) cm\(^{-3}\) contacts the aqueous side, and the amount of holes will accumulate on the CuO side, and electrons on the aqueous side. Hole carriers will capture OH\(^-\) adsorbed on the CuO film to form hydroxyl radicals OH\(^*\) (\( \text{h}^- + \text{OH}^- \rightarrow \text{OH}^* \)), until stabilized and built-in field is formed. Similar to the discussion in ref 23, CuO active layer under visible light illumination will generate electron–hole pairs, and the electron–hole pairs will be separated by the internal built-in potential formed at the CuO/electrolyte interface, where the electrons from the conduction band of CuO will reduce the hydroxyl radicals OH\(^*\) to OH\(^-\) anions (\( \text{e}^- + \text{OH}^* \rightarrow \text{OH}^- \)) at the CuO/electrolyte interface, thereupon the separated holes move from the CuO valence band through the FTO into the external circuit and then come back to the Pt layer. In this manner, the circuit has been completed. In ref 13, the authors found that the photocurrent is annealing temperature-dependent, where CuO film under a higher annealing temperature revealed an enhanced photocurrent because of the improved film crystallinity. Here, the air-annealed CuO film revealed an improved photocurrent performance due to its fewer localized oxygen at the sites of contact of nanoparticle and strong light absorption.

Figure 4. Photocurrent responses under on/off of 20 s at 0.0 V vs Ag/AgCl with illumination of 564 ± 60 nm 120 mW/cm\(^2\) incident intensity with samples \#2, \#3, and \#4 as photocathode (a); samples \#air, \#O\(_2\), and \#Ar as photocathode (b); transient decay times (c); decaying edges (d); photocurrent response for different incident intensities (e); and the relation between photocurrent \( I \) and incident intensity \( P \), \( \propto P^{\theta} \), with \( \theta \approx 0.59 \) (f).

Figure 5. Capacitive \( J \) versus scan rate for samples \#Ar, \#air, and \#O\(_2\).
CONCLUSIONS

CuO films on FTO substrate were prepared and annealed at air, oxygen, and argon flow atmospheres. All of the CuO films are composed of vertically arrayed CuO nanosheets, each individual nanosheet with a thickness of 100–500 nm. The prepared samples were used as photocathodes in the photoelectrochemical cell (PEC) to study the changes of the photocurrent performance. Those hierarchical CuO photodelectodes in the PEC exhibit quite different photoelectrochemical performance in visible light, as the annealed CuO films under air, oxygen, and argon atmospheres have photocurrents of 120, 17.5, and 3.5 μA, respectively. And an acceptor concentration of $2.9 \times 10^{21}$ cm$^{-3}$ was obtained for sample #air from the Mott–Schottky analysis, which is more than 2 times larger than that of #O$_2$ and 37 times larger than that of Ar. XPS and UPS measurements showed that more localized oxygen at the sites of nanoparticles’ contact resulted in a decrease in the carrier concentration and a decrease in the Fermi level. At the same time, sample #air can absorb more light. Therefore, high carrier concentration and strong light absorption determined the improved photocurrent performance. In addition to the annealing temperature, different annealing atmosphere gases are also important for the properties of the oxide semiconductors. The results obtained in this paper may be helpful to the preparations and application of nano-oxide semiconductors.

Table 2. Energy Level

| samples | $E_g$ (eV) | $E_C$ (eV vs vacuum) | $E_F$ (eV vs vacuum) | $E_V$ (eV vs vacuum) |
|---------|------------|----------------------|----------------------|----------------------|
| #air    | 1.31       | 4.05                 | 4.92                 | 5.36                 |
| #O$_2$  | 1.29       | 4.18                 | 4.92                 | 5.47                 |
| #Ar     | 1.29       | 4.18                 | 4.92                 | 5.47                 |

Scheme 2. Proposed Energy Band Alignment of the CuO/FTO Electrode

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Notes

The authors declare no competing financial interest.

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Figure 6. Mott–Schottky plots at fixed frequencies of 1 kHz on CuO photoelectrode registered in 0.1 M Na$_2$SO$_4$ electrolyte (pH 7) for three samples #air, #O$_2$, and #Ar (a, b); UPS data (c) view of the secondary electron edge (SEE); and (d) view of the valence band maximum (VBM) region.

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REFERENCES

(1) Masudy-Panah, S.; Moakhar, R. S.; Chua, C. S.; Kushwaha, A.; Wong, T. I.; Dalapati, G. K. Rapid Thermal Annealing Assisted Stability and Efficiency Enhancement in a Sputter Deposited CuO Photocathode. RSC Adv. 2016, 6, 29383–29390.

(2) Uchiyama, H.; Isobe, K.; Kozuka, H. Preparation of Porous CuO Films from Cu(NO)₂₃ Aqueous Solutions Containing Poly (vinylpyrrolidone) and Their Photocathodic Properties. RSC Adv. 2017, 7, 18014–18018.

(3) Cardiel, A. C.; McDonald, K. J.; Choi, K. S. Electrochemical Growth of Copper Hydroxy Double Salt Films and Their Conversion to Nanostructured p-Type CuO Photocathodes. Langmuir 2017, 33, 9262–9270.

(4) Hsu, Y. K.; Yu, C. H.; Chen, Y. C.; Lin, Y. G. Hierarchical Cu₂O Photocathodes with Nano/microstructures for Solar Hydrogen generation. RSC Adv. 2012, 2, 12455–12459.

(5) Banet, P.; Zhao, Y. P. Tuning the Cu₂O Nanorod Composition for Efficient Visible Light Induced Photocatalysis. Catal. Sci. Technol. 2016, 6, 2228–2238.

(6) Toupin, J.; Strub, H.; Kressmann, S.; Boudot, M.; Artero, V.; Laberty-Robert, Ch. Engineering n–p Junction for Photo-electrochemical Hydrogen Production. Phys. Chem. Chem. Phys. 2017, 19, 30675–30682.

(7) Baran, T.; Wojtysla, S.; Lenardi, C.; Vertova, A.; Ghigna, P.; Achilli, E.; Fracchia, M.; Rondinini, S.; Minguzzi, A. An Efficient CuO Photocathode for Hydrogen Production at Neutral pH: New Insights From Combined Spectroscopy and Electrochemistry. ACS Appl. Mater. Interfaces 2016, 8, 21250–21260.

(8) Guillen, C.; Herrero, J. Single-phase Cu₂O and CuO Thin Films Obtained by Low-Temperature Oxidation Processes. J. Alloys Compd. 2018, 737, 718–724.

(9) La, D. D.; Thi, H. P. N.; Kim, Y. S.; Rananaware, A.; Bhosale, S. V. Facile Fabrication of Cu(II)-Porphyrin MOF Thin Films From Tetrakis (4-Carboxyphenyl) Porphyrin and Cu(OH) Nanoneedle array. Appl. Surf. Sci. 2017, 424, 145–150.

(10) Hong, Q. S.; Cao, Y.; Xu, J.; Lu, H. M.; He, J. H.; Sun, J. L. Self-Powered Ultrafast Broadband Photodetector Based on p–n Heterojunctions of CuO/Si Nanowire Array. ACS Appl. Mater. Interfaces 2014, 6, 20887–20894.

(11) Jang, Y.; Jang, J. W.; Lee, J. S.; Choi, S. H.; Kim, J. Y.; Kim, J. H.; Youn, D. H.; Kim, W. Y.; Han, S. Tree Branch-shaped Cupric Oxide for Highly Effective Photoelectrochemical Water Reduction. Nanoscale 2015, 7, 7624–7631.

(12) Pauly, N.; Tougaard, S.; Yubero, F. Determination of the Cu 2p Primary Excitation Spectra for Cu, Cu₂O and CuO. Surf. Sci. 2014, 620, 17–22.

(13) Masudy-Panah, S.; Moakhar, R. S.; Chua, C. S.; Kushwaha, A.; Dalapati, G. K. Stable and Efficient CuO Based Photocathode through Oxygen-Rich Composition and Au – Pd Nanostructure Incorporation for Solar- Hydrogen Production. ACS Appl. Mater. Interfaces 2017, 9, 27596–27606.

(14) Dupin, J.-C.; Gonbeau, D.; Vinatier, P.; Levasseur, A. Systematic XPS Studies of Metal Oxides, Hydroxides and Peroxides. Phys. Chem. Chem. Phys. 2000, 2, 1319–1324.

(15) Stadnichenko, A. I.; Sorokin, A. M.; Boronin, A. I. XPS, UPS, and STM studies of nanostructured CuO films. J. Struct. Chem. 2008, 49, 341–347.

(16) Szuber, J.; Czempek, G.; Larciprete, R.; Koziej, D.; Adamowicz, B. XPS study of the L-CVD Deposited SnO₂ Thin Films Exposed to Oxygen and Hydrogen. Thin Solid Films 2001, 391, 198–203.

(17) Katic, J.; Hukovic, M. M.; Saric, I.; Petrovic, M. Semiconductor Properties of the Oxide Films Formed on Tin: Capacitive and XPS Studies. J. Electrochem. Soc. 2016, 163, C221–C227.

(18) Hafeldt, A.; Lindström, H.; Södergren, S.; Lindquist, S. E. Photoelectrochemical studies of colloidal TiO₂ films: The effect of oxygen studied by photocurrent transients. J. Electroanal. Chem. 1995, 381, 39–46.

(19) Zhang, H. F.; Cheng, C. W. Three-Dimensional PTO/TiO₂/BiVO₄ Composite Inverse Opals Photoanode with Excellent Photoelectrochemical Performance. ACS Energy Lett. 2017, 2, 813–821.

(20) Baran, T.; Wojtysla, S.; Lenardi, C.; Vertova, A.; Ghigna, P.; Achilli, E.; Fracchia, M.; Rondinini, S.; Minguzzi, A. An Efficient CuO Photocathode for Hydrogen Production at Neutral pH: New Insights From Combined Spectroscopy and Electrochemistry. ACS Appl. Mater. Interfaces 2016, 8, 21250–21260.

(21) Zhang, Z.; Yates, J. T. Direct Observation of Surface-Mediated Electron–Hole Pair Recombination in TiO₂ (110). J. Phys. Chem. C 2010, 114, 3098–3101.

(22) Mallows, J.; Planells, M.; Thakare, V.; Bhosale, R.; Ogale, S.; Robertson, N. p-Type NiO Hybrid Visible Photodetector. ACS Appl. Mater. Interfaces 2015, 7, 27597–27601.

(23) Xia, W. W.; Qian, H. Y.; Zeng, X. H.; Dong, J.; Wang, J.; Xu, Q. Visible-Light Self-Powered Photodetector and Recoverable Photocatalyst Fabricated from Vertically Aligned SnO₂ Nanoflakes on Carbon Paper. J. Phys. Chem. C 2017, 121, 19036–19043.