Lawrence Berkeley National Laboratory
Recent Work

Title
Rapid Flame-Annealed CuFe2O4 as Efficient Photocathode for Photoelectrochemical Hydrogen Production

Permalink
https://escholarship.org/uc/item/3ch7v42h

Journal
ACS Sustainable Chemistry and Engineering, 7(6)

ISSN
2168-0485

Authors
Park, S
Baek, JH
Zhang, L
et al.

Publication Date
2019-03-18

DOI
10.1021/acssuschemeng.8b05824

Peer reviewed
Rapid Flame-Annealed CuFe$_2$O$_4$ as Efficient Photocathode for Photoelectrochemical Hydrogen Production

Sangwook Park, Ji Hyun Baek, Liang Zhang, Jae Myeong Lee, Kevin H. Stone, In Sun Cho, Jinghua Guo, Hyun Suk Jung, and Xiaolin Zheng

ABSTRACT: Copper ferrite (CuFe$_2$O$_4$) possesses an indirect bandgap in the range of 1.54–1.95 eV. It is used as an attractive p-type photocathode in photo-electrochemical (PEC) water splitting, and theoretically it can yield a maximum photocurrent density of $\sim$27 mA/cm$^2$ and a maximum solar-to-hydrogen conversion efficiency of $\sim$33%. To date, only a few reports have been published on CuFe$_2$O$_4$ photocathodes with very low-photocurrent densities, with a maximum value of 0.4 mA/cm$^2$ at 0.4 V vs RHE. Herein, we prepared a CuFe$_2$O$_4$ photocathode on FTO glass with the sol–gel method followed by either high-temperature flame annealing or furnace annealing. We found that the flame-annealed CuFe$_2$O$_4$ photocathode generated a photocurrent density of 1.82 mA/cm$^2$ at 0.4 V vs RHE that is approximately 3.5 times higher than the furnace-annealed CuFe$_2$O$_4$ (0.52 mA/cm$^2$). This photocurrent density is also higher than those of all the reported CuFe$_2$O$_4$ photocathodes, and any Cu containing ternary oxide (Cu–M–O, M: Fe, Bi, V, and Nb) photocathode (0.1–1.3 mA/cm$^2$ at 0.4 V vs RHE). An improved PEC performance of the flame-annealed CuFe$_2$O$_4$ photocathode is elicited owing to the beneficial effects of flame annealing on the physical, optical, and electrical properties of CuFe$_2$O$_4$. Flame annealing enhances the light absorption property of the CuFe$_2$O$_4$ photocathode by slightly reducing the bandgap, and by forming a thicker film with increased porosity. Flame annealing also reduces the oxygen vacancy concentration in CuFe$_2$O$_4$, thus facilitating charge transport and interfacial charge transfer processes. Moreover, flame annealing requires only 16 min, which is much shorter than the time required for furnace annealing (~9 h). These results demonstrate that flame annealing is a rapid and effective means for fabricating metal oxide photoelectrodes with an enhanced PEC water splitting performance.

INTRODUCTION

Photoelectrochemical (PEC) water splitting has been extensively studied as a possible hydrogen production technique that utilizes solar energy to split water. A potential bias-free PEC configuration could be represented by the tandem cell that consists of p-type photocathodes and n-type photoanodes. There is a general consensus for inexpensive, active, and stable n-type photoanode materials, such as BiVO$_4$, WO$_3$, Fe$_2$O$_3$, and TiO$_2$. In comparison, there is lack of suitable p-type photocathode candidates. Good candidates for photocathodes are copper-based metal oxides because they are mostly nontoxic and cost-effective. For example, CuO and Cu$_2$O photocathodes have been used for PEC water reduction and have elicited good performance but poor stability. In addition, CuFe$_2$O$_4$, CuBi$_2$O$_6$, Cu$_3$VO$_4$, and CuNb$_2$O$_6$ photocathodes have been shown to have modest performance and stability.

Copper ferrite (CuFe$_2$O$_4$) is another p-type semiconductor in the family of copper-based metal oxides. CuFe$_2$O$_4$ has several attractive properties that makes it a possible candidate for photocathodes. CuFe$_2$O$_4$ has a narrow indirect bandgap in the range of 1.54–1.95 eV, thus yielding a theoretical maximum photocurrent density of $\sim$27 mA/cm$^2$ and a maximum solar-to-hydrogen conversion efficiency of $\sim$33%. CuFe$_2$O$_4$ has a conduction band minimum that is suitable for hydrogen evolution reactions. In fact, several studies have tested CuFe$_2$O$_4$ in photocathodes for PEC hydrogen evolution, but its elicited performance has been poor. Diez-Garcia et al. coated commercial, cubic CuFe$_2$O$_4$ nanoparticles with 30 nm which possessed a high-
degree of crystallinity on fluorine-doped tin oxide (FTO) glass substrate, followed by annealing at 450 °C for 1 h and electrochemical pretreatment. This CuFe2O4 photocathode finally attained a film thickness of 14 μm and achieved a current density of −40 μA/cm² at 0.75 V vs RHE.32 Li et al. grew cubic spinel structure of CuFe2O4 nanoparticle with average diameters in the range of 50−60 nm using the hydrothermal method followed by the coating of the particles on FTO and annealing at 400 °C for 2 h. This CuFe2O4 photocathode has a PEC performance of −0.4 mA/cm² at 0.4 V vs RHE.36 Among the various factors that account for the poor performances of these CuFe2O4 photocathodes was the poor contact between CuFe2O4 and FTO, as CuFe2O4 was coated on FTO with moderate post sintering temperature in the range of 400−450 °C. Better interface can be achieved by directly growing CuFe2O4 on the FTO substrate. The challenge is attributed to the fact that the crystallization temperature of CuFe2O4 (800−1000 °C) is much higher than the glass transition temperature of FTO (∼564 °C).

Herein, we apply our rapid and high-temperature flame annealing method (>980 °C)12,14,15,38−40 to anneal CuFe2O4 precursor films coated on FTO glass to prepare CuFe2O4 photocathode with high crystallinity and good contact with FTO glass. For comparison, we also prepared a control sample of a CuFe2O4 film which was coated on FTO glass after it was annealed in a conventional box furnace at 750 °C. The flame-annealed CuFe2O4 photocathode elicited a photocurrent density which was ∼3.5 times higher (∼1.82 mA/cm²) than that of furnace-annealed CuFe2O4 (∼0.52 mA/cm²) at 0.4 V vs RHE under 1 sun illumination in Ar purged 1 M NaOH electrolyte. The enhanced PEC performance of the flame-annealed CuFe2O4 photocathode was attributed to several reasons, as described next. First, flame annealing makes the CuFe2O4 film more porous and thicker that

| Table 1. Summary of Various Cu-Based Ternary Oxide Photocathodes |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|
|                                   | \( J_{ph} \) @ 0.4 V_RHE (mA/cm²) | \( J_{dark} \) @ 0.4 V_RHE (mA/cm²) | \( V_{onset} \) (VRHE) | \( \text{electrolyte} \) | \( \text{thickness} \) (μm) | \( \text{stability}^d \) | \( \text{ref} \) |
| CuFe2O4 (flame)                  | −1.82           | −0.35           | 1.05            | Ar purged 1 M NaOH | 530 nm            | 600s @ 0.15 V_RHE in Ar purged 1 M NaSO₄ | this work |
| CuFe2O4 (furnace)                | −0.52           | −0.15           | 0.85            | Ar purged 1 M NaOH | 450 nm            | 450s @ 0.15 V_RHE in Ar purged 1 M NaSO₄ | this work |
| CuFe2O₄                          | −0.04⁺          | −0.0              | 1.1             | N₂ purged 0.1 M NaOH | 14 μm            | −                       | 32 |
| CuFe₂O₄                          | −0.4            | −0.25           | 0.5             | 0.2 M Na₂SO₄      | 60 nm NPs         | over 240 s @ −0.2 V_SCE | 36 |
| CuFeO₂                           | −1.25           | −0.25           | 0.9             | O₂ purged 1 M NaOH | 290 nm            | over 600 s⁻¹ | 23 |
| CuFeO₃                           | −0.3            | −0.1           | 0.81            | Ar purged 1 M NaOH | 130 nm            | 70s @ 0.6 V_RHE | 24 |
| CuFeO₃                           | −1.3            | −0.2           | 0.8             | Ar purged 1 M NaOH | 6 times spin coating | 20 min w/NiFe/RGO in Ar purged 1 M NaOH | 25 |
| CuFeO₄                           | −0.8³           | −0.0              | 1.25            | 1 M NaOH          | over 1 μm         | over 1 h @ 0.6 V_RHE | 26 |
| Cu₃VO₄                           | −0.77⁷          | −0.55           | 0.2 V_SCE       | 0.5 M Na₂SO₄      | 1 μm              | 250s w/CuO NPs | 28 |
| CuBi₂O₆                          | −0.25           | −0.1           | 0.78            | CO₂ purged 0.1 M NaHCO₃ | 20 nm NPs         | −                       | 29 |
| \(^a\)At −0.2 V vs Ag/AgCl. \(^b\)At 0.6 V vs RHE. \(^c\)At −0.18 V vs SCE. \(^d\)Time for \( J_{ph} \) to be halved from its initial value. \(^e\)With AZO/TiO₂/Pt @ 0 V_RHE in Ar purged 0.5 M Na₂SO₄. |

Figure 1. Schematic of CuFe2O4 on FTO annealed by furnace and flame. (a) Illustration of the furnace annealing conditions and the dense film structure of the CuFe2O4 (furnace) on FTO. (b) Illustration of the flame annealing conditions and the porous film structure of the flame-annealed CuFe2O4 on FTO. (c, d) SEM images of top (c) and cross (d) view of CuFe2O4 on FTO (furnace). (e, f) SEM images of top (e) and cross (f) view of CuFe2O4 on FTO (flame).
after each spin coating, and the optimized thickness was achieved

1a), the samples were annealed in a box furnace at 450

by employing a solar simulator (Model LCS-100, Newport), and the

if not speci

spectra of CuFe₂O₄

increases light absorption in the visible light region (400–700

nm), and increases the surface area. Second, flame-

annealed CuFe₂O₄ has fewer oxygen vacancies, thus leading to

more efficient charge transport and transfer processes. Third, flame-annealed CuFe₂O₄ has a slightly smaller optical bandgap that extends the range of light absorption. Additionally, the flame annealing method shortens the annealing time from ~9 h to 16 min. To the best of our knowledge, the photocurrent density of our flame-annealed CuFe₂O₄ is higher than all the reported Cu-based ternary oxide photocathodes (Table 1).

EXPERIMENTAL SECTION

Synthesis of CuFe₂O₄ Film on FTO Substrate by Flame and Furnace. All samples were prepared on fluorine-doped tin oxide (FTO) coated-glass substrates (TEC 7, 7–8 Ω/sq, MSE Supplies). The FTO substrates were cleaned in acetone, IPA, and DI water, with sonication for 15 min, and were dried by an air gun. The CuFe₂O₄ precursor was prepared by the sol–gel method and was spin-coated on FTO glass for both annealing methods (see Supporting Information) at 3000 rpm for 60 s. The samples were then dried on a hot plate at 100 °C for 10 min. For furnace annealing (Figure 1a), the samples were annealed in a box furnace at 450 °C in air for 1 h after each spin coating, and the optimized thickness was achieved after five spin coatings. The samples are finally annealed at 750 °C for 20 min. For flame annealing (Figure 1b), the samples were annealed in an oxygen-rich postflame region at 980 °C for 2 min after each spin coating until all the five layers were optimized, followed by the final annealing at 980 °C for 8 min. Flame annealing was employed using a coflow premixed flat flame burner (McKenna Burner). The flow rates of CH₄ and air were set to 2.05 and 31.3 SLPM so that the fuel to oxygen equivalence ratio (Φ) was 0.63.

Photoelectrochemical Characterization. The PEC performances were measured in a standard three-electrode PEC cell using a Gamry 1000 potentiostat. The CuFe₂O₄ samples were used as the working electrodes with a glassy carbon as the counter electrode and Ag/AgCl reference electrode. Argon purged 1 M sodium hydroxide (NaOH) electrolyte (pH ~ 13.5) was used in all PEC measurements if not specified otherwise. All the PEC measurements were performed by employing a solar simulator (Model LCS-100, Newport), and the intensity was calibrated for a standard 1 sun condition (AM 1.5 G, 100 mW/cm²) using a photovoltaic reference (Model 91150 V, Newport). Electrochemical impedance spectroscopy (EIS) measurements were performed in the same, standard three-electrode configuration, using a potentiostat (SP200, Biologic) using 1 sun illumination. The incident photon-to-current conversion efficiency (IPCE) was measured at 0.4 V vs RHE with the use of a 150 W xenon arc lamp source (ABET Technologies) and a monochromator (Mmic 200, 600 gr/mm blazed at 500 nm) with a standard silicon photodiode cell.

RESULTS AND DISCUSSION

Methodological Differences between Furnace and Flame Annealing. As shown in Figure 1a,b, the main differences between furnace and flame annealing methods are the annealing temperature and duration. There is an upper annealing temperature limit for FTO glass as its glass transition temperature is approximately 564 °C, and its conductivity decreases when annealed at a temperature above 800 °C. Furnace annealing provides a homogeneous temperature environment, and our test shows that furnace annealing at 750 °C for 20 min is the upper temperature limit before severe FTO sheet resistance effects are documented. In contrast, many of our previous studies have demonstrated that flame annealing provides a heterogeneous temperature field. The coated materials on FTO (e.g., CuFe₂O₄ precursors) are exposed to high temperature but most of FTO glass is kept at a lower temperature due to large spatial temperature gradient, thus protecting its integrity and conductivity. The sheet resistances of FTO before and after flame annealing are close to the pristine value provided by vendor (Figure S1), confirming little impact on FTO from flame annealing. In addition, flame annealing not only enables the use of higher temperatures but also allows negligible ramping/cooling rates compared to the furnace. Therefore, flame annealing dramatically reduces the annealing time from ~9 h (furnace) to 16 min (flame).
Morphological Comparison of CuFe2O4 Photocathodes Annealed by Furnace and Flame. We first investigated how the furnace and flame annealing methods affect the morphology of CuFe2O4 thin films coated on FTO glass. SEM images show the morphology of the CuFe2O4 film annealed by furnace (Figure 1c,d) and flame (Figure 1e,f). The CuFe2O4 (furnace) film is very dense (∼450 nm) with connected grains, while the CuFe2O4 (flame) is porous and thicker (∼530 nm). The greater porosity and thickness of the CuFe2O4 (flame) enhances its light absorption response and increases its contact area with the electrolyte, yet both factors improve the PEC performance, as discussed below.

X-ray Characterizations of CuFe2O4 Annealed by Furnace and Flame. The crystallinity of CuFe2O4 (flame and furnace) film was examined by X-ray diffraction (XRD) as shown in Figure 2a. The XRD data of both CuFe2O4 films match the standard CuFe2O4 spectra (JCPDS, #34-0425), thus confirming the successful crystallization of the tetragonal copper ferrite phase that is a higher performance structural phase for high-performance photocatalysts.32 Figure S2 shows that the CuFe2O4 phase, which annealed at 450 °C for 1 h, is amorphous, thus confirming the need for high-temperature annealing for its crystallization.

To better understand the chemical states of CuFe2O4 (flame and furnace), we performed Cu and Fe K-edge X-ray absorption near-edge structure (XANES) experiments. The Cu K-edge XANES spectra of CuFe2O4 synthesized by furnace and flame annealing are shown along with the reference sample spectra of Cu foil and CuO in Figure 2b. The spectra of both CuFe2O4 samples show a peak at 8,997 eV (orange arrow) and have an edge rising position of ∼8,980 eV (gray arrow), thus indicating the absence of Cu1+ cations and the occupancy of the octahedral sites of Cu3+ cations.25,47 The Fe K-edge XANES spectra of both CuFe2O4 samples (Figure 2c) yielded a pre-edge peak at 7,114 eV (purple arrow), which is the characteristic feature of Fe3+ cations in the tetrahedral sites.47 The pre-edge peak is attributed to the transition from 1s to 3d, which is dipole-forbidden for the absorbers in a centrosymmetric environment.48 The enhancement of the pre-edge peak in the Fe K-edge XANES spectra is owing to the breaking of the symmetry owing to the noncentrosymmetric tetrahedral crystal field of Fe3+ cations in CuFe2O4.

The XANES spectra analysis revealed a minor difference between flame- and furnace-annealed CuFe2O4 samples. We then performed extended X-ray absorption fine structure (EXAFS) measurements to compare the local atomic structure of CuFe2O4 (flame and furnace). Figure 2d,e shows the Fourier transformed (FT) curves of Cu and Fe K-edge EXAFS spectra, respectively. For the Cu K-edge FT curves, the first peak at 1.45 Å originates from the Cu–O bond,47,49 and the second peak at 2.57 Å is ascribed to the bonds of Cu–Fe and Cu–Cu with both cations occupying the octahedral sites.47,49 The CuFe2O4 (flame) elicits a higher intensity for the first peak (Cu–O bond), while the CuFe2O4 (furnace) has a higher intensity for the second peak (Cu–Fe and Cu–Cu bonds). This difference suggests that the CuFe2O4 (flame) has fewer oxygen vacancies.49 The Fe K-edge results yielded a similar behavior in that CuFe2O4 (flame) shows a higher relative intensity for the first peak (Fe–O bond) than the second peak (Fe–Cu and Fe–Fe) compared with those of CuFe2O4 (furnace).47,49 The difference in the oxygen vacancy between CuFe2O4 films by flame and furnace is expected to affect their electronic properties and performance for PEC hydrogen production (Figure S3).

Electronic Band Structure Comparison of CuFe2O4 Annealed by Furnace and Flame. The electronic structures of the CuFe2O4 (flame and furnace) films were investigated by UV–vis spectroscopy and ultraviolet photoelectron spectroscopy (UPS). The UV–vis spectroscopy determined the band gap from the Tauc plot method (Figure 3a). The Tauc plots show that both CuFe2O4 (flame and furnace) films have an indirect bandgap, as shown in the inset of Figure 3a. The CuFe2O4 (flame) has a slightly smaller optical bandgap (1.84 eV) than that of CuFe2O4 (furnace, 1.95 eV). The CuFe2O4 (flame) and CuFe2O4 (furnace) have theoretical photocurrent density limits of ∼17.5 and ∼15.3 mA/cm², respectively, which were calculated based on reference solar spectral irradiances (AM1.5, ASTM G173, NREL). The bandgap values are close to the previously reported bandgap range of CuFe2O4 from 1.54 to 1.80 eV.30–35 Moreover, the CuFe2O4 (flame) had a higher light absorption efficiency than CuFe2O4 (furnace) over the wavelength range from 400 to 700 nm (Figure S5), which is a consequence of its higher porosity and thickness (Figure 1c–f).

The UPS measurement (Figure S6) was used to determine the work function and the valence band maximum (VBM) of CuFe2O4. The band positions and band edge values for CuFe2O4 (flame and furnace) were estimated by UPS
measurements, as shown in Figure 3b. According to the UPS and UV–vis data, the calculated conduction band minimum values of CuFe$_2$O$_4$ (flame and furnace) films are $-0.69$ and $-0.92$ V vs NHE, and the maximum values of the valence band are $1.15$ and $1.03$ V vs NHE, respectively (see the Experimental Section for details). The obtained band structures confirmed that the CuFe$_2$O$_4$ photocathodes synthesized by flame and furnace annealing were thermodynamically favorable to drive the hydrogen evolution reaction.

**Photoelectrochemical Characterizations of CuFe$_2$O$_4$ Annealed by Furnace and Flame.** Figure 4a shows the linear sweep voltammetry of CuFe$_2$O$_4$ (flame and furnace) in Ar purged 1 M NaOH electrolyte in the dark (dashed lines), and under 1 sun illumination (solid lines). These polarization curves were constructed with a scan rate of 10 mV/s. Correspondingly, the current density values were calculated based on the projected area of the FTO glass substrate. The thickness of the CuFe$_2$O$_4$ film had been optimized based on the photocurrent density values under 1 sun illumination (Figure S7). The optimal thickness is shown in Figure 1d.f.

The CuFe$_2$O$_4$ (flame) clearly elicited a better PEC performance than CuFe$_2$O$_4$ (furnace) with an earlier onset and a higher photocurrent density in the range of the voltage sweep. The CuFe$_2$O$_4$ (flame) photocathode exhibited a positively shifted onset potential of $\sim 1.05$ V vs RHE, in comparison to that of the CuFe$_2$O$_4$ (furnace) of $\sim 0.85$ V vs RHE. This characteristic establishes the CuFe$_2$O$_4$ (flame) as a better photocathode for coupling with the photoanode in a PEC tandem cell.

The improved PEC performance of CuFe$_2$O$_4$ (flame) photocathode is only partially caused by its enhanced light
absorption property in the visible light region (Figure S5) owing to its thicker and more porous film morphology. In addition, we further conducted electrochemical impedance spectroscopic (EIS) analyses to compare the effect of furnace and flame annealing on the charge transport and transfer efficiency. The EIS data were measured at 0.4 V vs RHE under 1 sun illumination were fitted to a circuit model, as specified in an inlet of Figure 4c. In this model, the resistances and capacitances are composed of a series resistance (R1) that describes the charge transport resistance at the interface between the CuFe2O4 film and the FTO substrate, a charge transfer resistance (R2) and a capacitance of the space charge region (C2) in the bulk of material, and a charge transfer resistance (R3) and a Helmholtz capacitance (C3) at the interface between the CuFe2O4 film and the liquid electrolyte. The fitted resistance values are listed in Table 2. First, the flame-annealed film has a better electrical contact between the CuFe2O4 film and the FTO substrate since the values of R1 of flame-annealed CuFe2O4 (19.46 Ω) is much smaller than that of furnace-annealed CuFe2O4 (156.8 Ω). In addition, the charge transport resistance of CuFe2O4 (flame) is lower (~11 kΩ) than that of CuFe2O4 (furnace, ~20 kΩ). This is attributed to the reduced oxygen vacancies from the EXAFS analysis in Figure 2d,e. Moreover, the charge injection resistance was dramatically reduced from ~667 kΩ for CuFe2O4 (furnace) to ~6 Ω for CuFe2O4 (flame) (Figure 4c). The EIS results indicate that flame annealing improves both the charge transfer and transport efficiencies, thus leading to the enhanced PEC performance of CuFe2O4 (flame).

Additionally, we measured the electrochemical active surface area (ECSA) to understand the charge transfer process. The capacitive currents were measured at 1.13 V vs RHE because of the possible Faradaic current in the potential range from 0.78 to 1.18 V vs RHE. Figure 4d plots the capacitive current as a function of scan rate for CuFe2O4 (flame and furnace) in which the slope is proportional to the ECSA ratio. The ECSA ratio of the CuFe2O4 based on flame and furnace is 2.78. The higher ECSA value of CuFe2O4 (flame) indicates a better interfacial charge transfer efficiency, which is consistent with the EIS results (Figure 4c).

Finally, the stability of the CuFe2O4 photocathode was tested using chronoamperometry using chopped illumination at 0.15 V vs RHE for 10 min in Ar purged 1 M Na2SO4 electrolyte in agreement with the J–V curves (Figure S9). The stability test was not conducted in 1 M NaOH but in 1 M Na2SO4 to reduce the chemical influence from the strong alkaline electrolytes. Both CuFe2O4 films by flame (red) and furnace (black) show acceptable stabilities, as compared to many reported Cu- and Fe-based ternary oxides (Table 1) and Cu2O without the use of any protective layers and electrocatalysts. The stability of the CuFe2O4 photocathode still needs to be further improved to be a practical photocathode. The main reason for the instability is the chemical reduction of Cu+ under the PEC bias range needed for hydrogen evolution reaction (Figures S10–S12). Potential methods for improving the stability of the CuFe2O4 include elemental doping, deposition of protection layers, addition of electrocatalysts, and a combination of them.

**CONCLUSIONS**

In summary, we investigated the potential of flame-annealed CuFe2O4 as a photocathode for PEC hydrogen production. The flame-annealed CuFe2O4 photocathode achieved a photocurrent density of ~1.82 mA/cm² at 0.4 V vs RHE that is higher than the photocurrent density of the furnace-annealed CuFe2O4, and the corresponding photocurrent density values of all the reported Cu-based ternary oxide photocathodes. The enhanced PEC performance of the flame-annealed CuFe2O4 photocathode was attributed to several factors. First, the flame-annealed CuFe2O4 film was more porous and thicker, and led to a better light absorption and a higher surface area. Second, the flame-annealed CuFe2O4 had fewer oxygen vacancies, and hence achieved more efficient charge transport and transfer processes. Third, flame-annealed CuFe2O4 had a slightly smaller optical bandgap that extended the range of light absorption. On top of that, the flame annealing method shortened the annealing time from ~9 h to 16 min. These results showed that the CuFe2O4 photocathode could elicit a good performance for PEC hydrogen production. Nevertheless, the stability of the CuFe2O4 photocathode is still not adequate and it has to be further improved for practical PEC water splitting.

**AUTHOR INFORMATION**

**Corresponding Authors**

S. Jung. E-mail: hsjung1@skku.edu. Fax: +82-31-290-7410. Phone: +82-31-290-7403.

X. Zheng. E-mail: xzheng@stanford.edu. Fax: +1-650-723-1748. Phone: +1-650-736-8953.

**ORCID**

Sangwook Park: 0000-0003-0939-1696
Liang Zhang: 0000-0002-3446-3172
In Sun Cho: 0000-0001-5622-7712
Jinghua Guo: 0000-0002-8576-2172
Hyun Suk Jung: 0000-0002-7803-6930
Xiaolin Zheng: 0000-0002-8889-7873
Author Contributions

These authors contributed equally to this work.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

X.Z. acknowledges generous financial support from the Stanford Woods Institute for the Environment and the Stanford Natural Gas Initiative for their generous support. This work was also supported by Basic Science Research Program through the National Research Foundation of Korea (No. 2017R1A2B3010927), Global Frontier R&D Program of the Center for Multiscale Energy System (2012M3A6A7054855), and Creative Materials Discovery Program (2016M3D1A1027664). Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences under Contract No. DE-AC02-76SF00515. J.G. used resources on BL8.0.1 of the Advanced Light Source, which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231.

REFERENCES

(23) Prevot, M. S.; Guijarro, N.; Sivula, K. Enhancing the Performance of a robust sol-gel-processed p-type delafossite CuFeO₂ photocathode for solar water reduction. ChemSusChem 2015, 8 (8), 1359–1367.


