Solution-Processed Synthesis of Copper Oxide (Cu$_x$O) Thin Films for Efficient Photocatalytic Solar Water Splitting

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ABSTRACT: This article reports a solution-processed synthesis of copper oxide (Cu$_x$O) to be used as a potential photocathode for solar hydrogen production in the solar water-splitting system. Cu$_x$O thin films were synthesized through the reduction of copper iodide (CuI) thin films by sodium hydroxide (NaOH), which were deposited by the spin coating method from CuI solution in a polar aprotic solvent (acetonitrile). The phase and crystallinity quality of the synthesized Cu$_x$O thin films prepared at various annealing temperatures were investigated using various techniques. The X-ray diffraction and energy dispersive X-ray spectroscopy studies confirm the presence of Cu$_2$O, CuO/Cu$_2$O mixed phase, and pure CuO phase at annealing temperatures of 250, 300, and 350 °C, respectively. It is revealed from the experimental findings that the synthesized Cu$_x$O thin films with an annealing temperature of 350 °C possess the highest crystallinity, smooth surface morphology, and higher carrier density. The highest photocurrent density of −19.12 mA/cm$^2$ at −1 V versus RHE was achieved in the photoelectrochemical solar hydrogen production system with the use of the Cu$_x$O photocathode annealed at a temperature of 350 °C. Therefore, it can be concluded that Cu$_x$O synthesized by the spin coating method through the acetonitrile solvent route can be used as an efficient photocathode in the solar water-splitting system.

1. INTRODUCTION

Energy consumption is increasing rapidly because of the increase in population and industrialization in the world. Production of hydrogen (H$_2$) as chemical energy using the abundant solar power can be an excellent resolution to this growing energy crisis. A simple technique to produce H$_2$ is water splitting in a photoelectrochemical (PEC) cell. In the PEC system, the photoelectrode is irradiated by sunlight, light is absorbed in the photoanode, and electron–hole pairs are generated, which are driven into the solution by the electric field at the photoanode/water junction to produce H$_2$ and oxygen (O$_2$) in the PEC water-splitting system. Efficient photoelectrode materials are selected based on some fundamental properties such as a high absorption coefficient, excellent charge transport capability, photocorrosion stability in the electrolyte solution, and low kinetic overpotentials. However, there is no single material that meets all the criteria for an efficient photoelectrode. Therefore, finding suitable materials for the absorption of a full portion of incident photons, developing active catalysts, and realizing the appropriate interface design between the catalyst, photo-absorber, and electrolyte to minimize losses are the main challenges for an efficient PEC system.

A number of photocatalysts including titanium oxide (TiO$_2$), zinc oxide (ZnO), tungsten oxide (WO$_3$), iron oxide (Fe$_3$O$_4$), bismuth vanadium tetra-oxide (BiVO$_4$), cuprous oxide (Cu$_2$O), and the more active catalyst cupric oxide (CuO) have been investigated for perceiving a high-efficiency PEC water-splitting system. Among these catalysts, copper oxides (CuO and Cu$_2$O) have recently attracted special attention because they are abundant in the crust of the earth, low-cost and nontoxic. Moreover, copper oxide photocathodes can be prepared using electro-deposition, spin coating, RF-magnetron sputtering, and spray pyrolysis techniques. Depending on the techniques and criteria of preparation, the direct band gap of the p-type Cu$_2$O and CuO has been observed to be nearly 2.0–2.5 and 1.3–1.7 eV, respectively. The band alignment of the Cu$_2$O and CuO is favorable for the generation of the H$_2$ fuel in the PEC system. The theoretical solar-to-hydrogen conversion efficiency of both Cu$_2$O and CuO is >18%.
However, the practical Cu2O photoelectrodes suffer from the poor-stability problem in the aqueous solution because its redox potential lies within the band gap. Surface passivation of the photocathodes through the use of conformal coating could be one possible way to enhance the stability of the Cu2O photoelectrodes. Low efficiency of the Cu2O photocathodes is another critical issue. The unfavorable minority carrier diffusion length and slow carrier transfer rate at the photocathode surface are the main issues for the practical copper oxide (Cu2O, CuO) photocathodes that are responsible for the low efficiency of the devices.

However, the performance of the copper oxide photocathode can be enhanced by improving the crystal quality and surface morphology of the material. To address this problem, researchers have applied different techniques such as doping and high-temperature treatment to copper oxide for the fabrication of an efficient PEC system. So far, the electrodeposited Cu2S-coated Cu2O NW photoelectrode has been reported to produce a photocurrent of −1.0 mA/cm² at −0.6 V versus Ag/AgCl. A photocurrent of 0.49 mA/cm² at −0.25 V versus Ag/AgCl has been reported for the electrodeposited Cu2O electrode with NiFe-layered double hydroxides. Son et al. also reported a photocurrent density of −5.2 mA/cm² at 0 V versus RHE for the electrodeposited Cu2O photocathode using Cu2O/NiO as a back protected layer. Lim et al. reported a photocurrent of −0.28 and −0.35 mA/cm² at 0.05 V versus RHE for the sol–gel deposited Cu2O and CuO photoelectrode, respectively. The RF-magnetron-sputtered CuO photocathode yielded a photocurrent of −3.1 mA/cm² at 0 V (RHE). A solution-processed CuO nanoparticle films provided a photocurrent of −1.2 mA/cm² at −0.7 V versus Ag/AgCl. Baran et al. reported a photocurrent of −1.3 mA/cm² at 0.2 V versus RHE for the solution-processed Cu2O photocathode. A photocurrent of −24 mA/cm² at 0.25 V versus RHE has also been reported for the spray-pyrolyzed tenorite CuO thin films.

In addition, the solution-processed synthesis of Cu2O thin films by the spin coating method could produce potential candidates as efficient photoelectrodes for application in solar hydrogen production as it reduces cost and fabrication complexity. Recently, a simple one-step synthesis of p-type Cu2O thin films via in situ reaction of a spin-coated CuI thin film in aqueous NaOH solution has been reported for the fabrication of efficient thin-film transistors. The Cu2O thin films synthesized by the same route have been used as a hole transport layer for the perovskite solar cells. Moreover, the deposition of CuI thin films by the spin coating method from a CuI solution dissolved in acetonitrile solvent has already been reported. However, there are few reports on the application of CuO photocathodes in PEC solar water splitting synthesized from the reduction of spin-coated CuI thin films.

In this article, we demonstrate the facile one-step synthesis of Cu2O thin films through the reduction of CuI thin films prepared from a CuI solution dissolved in acetonitrile by the spin coating method for the efficient application in the solar water-splitting system. The synthesized Cu2O thin films as a photocathode exhibited excellent performance in the PEC solar water-splitting system with better reproducibility. It is revealed from the findings that the acetonitrile-assisted synthesized Cu2O thin film could be a deserving candidate as a photocathode in the PEC system for solar H2 production by water splitting.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction and TGA–DTA Studies of Copper Oxide Thin Films. The photocatalytic performance of a photocathode is dependent on the phase purity and crystallinity of the materials used as an electrode. The phase and crystallinity of the synthesized Cu2O thin films were determined by X-ray diffraction (XRD) analysis. The XRD pattern of the Cu2O thin films annealed at different temperatures is depicted in Figure 1a. For the film annealed at 250 °C, the peaks at 36.52 and 42.44° are corresponding to (111) and (200) diffraction planes of the face centred cubic (fcc) Cu2O crystalline structure (JCPDS Card no. 65-3288). This result indicates that a well-crystallized Cu2O film with no CuO phase formed at an annealing temperature of 250 °C. The phase change of the film from Cu2O to CuO was revealed at an annealing temperature of 300 °C. The XRD peaks at 2θ of 35.7, 38.9, and 49° for the film annealed at 300 °C corresponding to (002), (111), and (−202) planes, respectively, are attributed to the monoclinic crystal structure of CuO (JCPDS Card no. 48-1548) with improved crystallinity. The presence of the Cu2O phase was also confirmed by the peak positioned at 61.53° with orientation to the (220) plane in the film annealed at 300 °C. On the other hand, only the CuO phase was confirmed for the film annealed at 350 °C, as observed in Figure 1a. The sharp peaks signify the improved crystallinity of the CuO film with no other phase of copper oxide after annealing at 350 °C. These results on the thermal oxidation behavior of Cu2O thin films are in good agreement with the reported work.
The crystallite size \( (D) \) of the synthesized Cu\(_x\)O thin films was calculated using the Debye–Scherrer formula and is shown in Table 1. It is found that the crystallite size increases with annealing temperature and the Cu\(_x\)O thin film annealed at 350 °C showed the highest crystallinity.

| annealing temperature (°C) | phase   | \((hlk)\) | \(2\theta\) (deg) | fwhm (deg) | crystallite size (nm) |
|----------------------------|---------|----------|-------------------|-----------|-----------------------|
| 250                        | Cu\(_x\)O (111) | 36.52    | 0.89              | 11.5      |                       |
|                            | Cu\(_x\)O (200) | 42.44    | 0.71              | 14.2      |                       |
| 300                        | CuO (002)    | 35.70    | 0.54              | 18.2      |                       |
|                            | CuO (111)    | 38.90    | 0.74              | 13.9      |                       |
|                            | CuO (−202)   | 49.00    | 0.71              | 16.7      |                       |
| 350                        | Cu\(_x\)O (220) | 61.53    | 0.91              | 18.4      |                       |
|                            | CuO (002)    | 35.70    | 0.48              | 20.4      |                       |
|                            | CuO (111)    | 38.90    | 0.54              | 18.6      |                       |
|                            | CuO (−202)   | 49.00    | 0.53              | 22.8      |                       |

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) are the popular methods to investigate the thermal stability of the semiconducting materials.\(^{46–49}\) Therefore, TGA and DTA of the Cu\(_x\)O thin film (preannealed at 120 °C) were carried out to determine the proper annealing temperature. The TGA–DTA spectra were taken by scanning the temperature from 30 to 500 °C at 20 °C/min under a continuous flow of nitrogen gas at 20 mL/min. Figure 1b delineates the TGA–DTA spectra of the copper oxide sample. About 22% weight loss appeared from temperature 273—400 °C with no weight loss found except for this range. Such a huge weight loss reveals the transformation of the Cu\(_2\)O phase to the CuO phase and the evaporation of other volatile elements. Further weight loss was not observed above 400 °C, indicating the thermal stability of Cu\(_x\)O from 400 to 500 °C. Therefore, the appropriate annealing temperature is >400 °C under a nitrogen atmosphere. Simultaneous thermal decomposition and improved crystallinity of the prepared sample appear from the DTA spectra. It also predicts that an optimum crystallinity of the sample could be obtained at a temperature of >400 °C.

2.2. Surface Morphological Study of Cu\(_x\)O Thin Films. Figure 2a–c illustrate the surface morphology of the synthesized Cu\(_x\)O thin films synthesized from the reduction of spin-coated CuI thin films in aqueous NaOH and annealed...
at different temperatures. The surface of the Cu$_x$O thin film annealed at 250 °C appears to be covered almost uniformly with grains of ~0.9 μm. Several void spaces were also observed in the film. The surface morphology of the film significantly changed for the films annealing at 300 °C. The grains of the 300 °C-annealed copper oxide were found to be randomly distributed. The increase in void spaces, grain boundaries, and the surface roughness of the films might be due to the phase transition of the copper oxide from Cu$_2$O to CuO and evaporation of the volatile elements. The nucleation rate was found maximum at 350 °C and ~0.34 μm grains were observed with a few amounts of grain boundaries. As shown in Figure 2c, the surface of the Cu$_x$O film annealed at 350 °C is very compact and smoother with reduced void spaces than compared to that of the films annealed at other temperatures. Improved surface morphology of the photocathode is favorable for the PEC performance, which resists the recombination of the charge carriers and benefits in the enhancement of the charge transport property.

2.3. Optical Properties of Cu$_x$O Thin Films. The optical properties of the synthesized Cu$_x$O thin films are shown in Figure 3. The absorption spectra of the Cu$_x$O thin films are depicted in Figure 3a. The absorbance increases with increasing annealing temperature. The Cu$_x$O thin film annealed at 350 °C showed better absorbance than other films that may arise because of large grain size, less void spaces, a smooth surface, and compactness of the film. The band gap of Cu$_x$O thin films was calculated using the Tauc plot, as shown in Figure 3b. It is reported that both Cu$_2$O and CuO are p-type semiconductors having direct and indirect optical band gap, respectively. It was revealed from the XRD and EDX studies that the films annealed at 250, 300, and 350 °C were the pure Cu$_2$O, Cu$_2$O/CuO mixed, and pure CuO phase, respectively. Therefore, the direct band gap

| annealing temperature (°C) | Cu (%)       | O (%)       | [Cu]/[O] |
|---------------------------|--------------|-------------|----------|
|                           | atomic %     | weight %    | error (%) | atomic %     | weight %    | error (%) | [Cu]/[O] |
| 250                       | 71.43        | 90.78       | 5.3       | 28.57        | 9.22        | 8.3       | 2.50 |
| 300                       | 55.56        | 83.11       | 5.5       | 44.44        | 16.89       | 8.2       | 1.25 |
| 350                       | 46.51        | 77.39       | 5.4       | 53.49        | 22.61       | 8.0       | 0.87 |

Figure 3. (a) Optical absorbance spectra and (b) Tauc plots of the synthesized Cu$_x$O thin films annealed at a temperature from 250 to 350 °C.

Figure 4. (a) MS plots of the Cu$_x$O thin films and (b) energy band diagram of the Cu$_2$O and CuO photocathodes at pH = 1.6.
of Cu$_2$O and Cu$_2$O/CuO thin films was calculated using \((ahu)^2\) versus \(h\nu\) plot, whereas \((ahu)^0.5\) versus \(h\nu\) plot was used for the calculation of the indirect band gap of Cu$_2$O thin films, as depicted in Figure 3b. The direct band gaps of Cu$_2$O and Cu$_2$O/CuO thin films were found to be 2.1 and 1.9 eV, respectively. On the other hand, the indirect band gap of Cu$_2$O thin films was found to be 1.3 eV. This observed band gap of Cu$_2$O thin films is consistent with the previous studies.\(^{54,55}\) It is also theoretically predicted that around 35 mA/cm$^2$ photocurrent could be produced by the CuO having a band gap of 1.3 eV.\(^{58}\)

### 2.4. Carrier Transfer Property of Cu$_2$O Thin Films

In the previously reported work, Cu$_2$O photocathodes exhibited very low solar-to-hydrogen conversion efficiency because of the poor carrier transfer property of the surface.\(^{29,33,50}\) Therefore, enhancement of the carrier transfer property of the Cu$_2$O photocathodes is of high demand to the researchers. The carrier transfer property and semiconducting nature of the synthesized Cu$_2$O thin films were determined from the Mott–Schottky (MS) plot, illustrated in Figure 4a. The MS plot of the Cu$_2$O thin films annealed at different temperatures was constructed using the capacitance–voltage data observed in the impedance analyzer. The carrier density \((N_D)\) was calculated using the following equation\(^{35}\)

$$\frac{1}{C^2} = \frac{2}{\varepsilon \varepsilon_0 A^2 e N_D} \left( V - V_{fb} - \frac{kT}{e} \right)$$

where \(C\) is the differential capacitance, \(\varepsilon\) is the dielectric constant of the semiconductor, \(\varepsilon_0\) is the permittivity of free space, \(N_D\) is the density of dopants, \(V\) is the applied potential, \(V_{fb}\) is the flat band potential, \(k\) is the Boltzmann constant, and \(T\) is the absolute temperature. The negative slope of the MS plot confirms the p-type conductivity of the Cu$_2$O thin films. The value of the flat band potential \((V_{fb})\) was calculated by the slope of the extrapolating linear part of the MS plot. The value of \(V_{fb}\) and the carrier concentration were found to vary from 1.04 to 1.16 V and 3.4 $\times$ 10$^{21}$ to 3.95 $\times$ 10$^{21}$ cm$^{-3}$ at the variation of annealing temperature from 250 to 350 °C, respectively. The films annealed at 350 °C show high carrier concentration, which might be the result of the better quality of the film, as revealed by the XRD and scanning transmission microscopy (SEM) studies. The enhancement of carrier concentration with annealing temperature signifies a high density of copper vacancies. The increase in charge carrier density promotes the degree of band bending at the Cu$_2$O, which promotes the charge separation at the Cu$_2$O/electrolyte interface.\(^{28}\)

Figure 4b shows the energy band diagram of the Cu$_2$O and CuO photocathodes, considering the band gap of 2.1 eV for Cu$_2$O and 1.3 eV for CuO. The reduction of proton (H$^+$) is in favor because the H$^+$/H$_2$ potential is more positive than the conduction band (CB) potential of both Cu$_2$O and CuO photocathodes.\(^ {59}\) The schematic diagram of the two-electrode PEC water-splitting system using the synthesized Cu$_2$O films as the working electrode (WE) and Pt as the counter electrode (CE) is also shown in the inset of Figure 4b. When the light is incident on the Cu$_2$O photocathode, the electron–hole pairs will be generated. The protons will be reduced at the Cu$_2$O/electrolyte interface by the CB electrons. Besides, oxidation of oxygen will occur at the CE because of the transfer of photogenerated holes from the Cu$_2$O photocathode to the CE.

### 2.5. Photocatalytic Performance of Cu$_2$O Thin Films

The current–voltage characteristics of the Cu$_2$O photocathodes in the three-electrode PEC water-splitting system are depicted in Figure 5a. The plot shows the photocurrent density of the best performing Cu$_2$O photocathodes among a number of samples with better reproducibility. First, the experimental potential was measured with respect to the Ag/AgCl reference electrode (RE). Then, the potential versus Ag/AgCl was converted into the potential versus RHE (reversible hydrogen electrode) scale with the help of the following formula

$$E_{RHE} = E_{Ag/AgCl} + 0.059pH + E_{0}^{Ag/AgCl}$$

where, \(E_{RHE}\) is the potential converted into the RHE scale, \(E_{Ag/AgCl}\) is the experimentally measured potential with respect to the Ag/AgCl reference electrode (RE), pH is the pH of the electrolyte, and \(E_{0}^{Ag/AgCl} = 0.1976\) V at 25 °C.

At an applied potential of −0.5 V versus RHE (onset potential), H$_2$ production was initiated from the photocathode annealed at 250 °C (production of bubbles), and the production of bubbles increased with increasing applied bias potential; the onset potential of −0.47 V versus RHE and −0.4 V versus RHE was observed for the photocathodes annealed at 300 and 350°C, respectively. The onset potential followed the variation of the flat band potential in a reversible way; a low onset potential is desirable for an efficient photocathode. The synthesized photocathode annealed at 250, 300, and 350 °C produced a photocurrent density of −12.50, −2.13, and −19.12 mA/cm$^2$, respectively, at −1 V versus RHE. As it was confirmed from the XRD and EDX results that Cu$_2$O thin films...
The CuO photocathode produced a higher photocurrent density than the Cu2O photocathode. The higher carrier mobility. The CuO photocathode helped to produce higher crystallite size, uniform surface morphology, and higher carrier photoelectrode in aqueous solution is low.

CuO/Cu2O, and CuO photocathodes, respectively, at −1V vs RHE. It is observed from Figure 5a that the photocathode annealed at 300 °C shows low photocurrent density than the other photocathodes. The presence of mixed copper oxide phases (CuO/Cu2O) in the film annealed at 300 °C might be the reason for the low photocurrent density because the mixed (nonstoichiometric) copper oxide phases induce more defects (trapping centers) and reduced the carrier mobility. The CuO photocathode produced a higher photocurrent than the Cu2O photocathode. The higher crystallite size, uniform surface morphology, and higher carrier density of the CuO photocathode helped to produce higher photocurrent than the Cu2O photocathode,

where \( V_i \) is the applied potential between the WE and CE in a two-electrode configuration and its corresponding photocurrent density is \( J_{ph} \) and \( P_{total} \) is the total light (100 mW/cm²) incident on the photocathode. As illustrated in Figure 5b, the optimum ABPE for the Cu2O, CuO/Cu2O, and CuO photocathodes is 4.69% (at 0.9 V vs Pt), 0.79% (at 0.9 V vs Pt), and 7.06% (at 0.85 V vs Pt), respectively. The observed PEC performance of the synthesized photocathodes is much higher than the previously reported performance. Table 3 shows a comparison of CuO-based photocathode performance with that of our synthesized CuO photocathode.

The objective of the present work was to synthesize an efficient CuO photocathode for the PEC system. Because the stability of the CuO photocathodes is an important issue, the stability of the photocurrent of the synthesized photocathodes was observed under 100 mW/cm² sun light conditions at −1 V versus Pt using the two-electrode system and is shown in Figure 6. Till now, the photostability of the CuO photocathodes is far from that of the typical photoelectrodes (WO3 and α-Fe2O3); the fast photocorrosion deactivated the CuO photocathodes.

It has been demonstrated that the copper oxides spontaneously decompose to metal Cu under illumination; Cu accumulated on the surface and deactivated the inner copper oxide after a certain period. It is observed from the Figure 6 that the photocathodes which were annealed at 250 (Cu2O), 300 (CuO/Cu2O), and 350 °C (CuO) retained about ~85% of their initial photocurrent for ~30, ~34, and ~39 min, respectively. After this period, the

Table 3. Comparison of CuO-Based Photocathode Performance Synthesized using Different Techniques

| photocathode          | thickness (nm) | fabrication technique          | photocurrent refs |
|-----------------------|----------------|-------------------------------|-------------------|
| NiO–CuO thin film     | 850            | sol–gel spin coating          | −1.07 mA/cm² at −0.55 V (Ag/AgCl) 24 |
| CuO thin film         | ~500           | sputtering                    | −0.65 mA/cm² at −0.45 V (Ag/AgCl) 66 |
| Li-doped CuO nanoparticles | 1700         | flame spray pyrolysis        | −1.7 mA/cm² at −0.55 V (Ag/AgCl) 27 |
| CuO thin film         | 500            | RF-magnetron sputtering       | −3.1 mA/cm² at 0 V (RHE) 67 |
| CuO nanoparticles     | 1340           | spin coating                  | −1.2 mA/cm² at −0.55 V (Ag/AgCl) 68 |
| CuO thin film with TiO2 protecting layer and Au–Pd co-catalyst nanostructures (CuO–TiO2–AuPd) | ~500 | sol–gel method and RF sputtering | −1.9 mA/cm² at 0 V vs RHE 69 |
| tenorite CuO thin films | ~500         | spray pyrolysis               | −24 mA/cm² at 0.25 V vs RHE 33 |
| Cu2O/CuO/C             | ~2000          | electrodeposition             | −7.5 mA/cm² at −0.1 V vs RHE 70 |
| CuO                    | ~700           | spin coating                  | −19.12 mA/cm² at −1 V vs RHE present work |

Figure 6. Photocurrent stability of the CuO photocathodes annealed at (a) 250, (b) 300, and (c) 350 °C measured using the two-electrode system.
Figure 7. Preparation steps of Cu$_x$O photocathodes.

Photocurrent was drastically suppressed because of photocorrosion. The Cu$_x$O photocathode annealed at 350 °C showed better stability against photocorrosion among the all synthesized Cu$_x$O photoelectrodes. However, many researchers have already tried to overcome the stability issue of the Cu$_x$O photocathodes through a successful way of using a surface protective layer on the Cu$_x$O photocathodes. Following the same strategy, future research could be conducted to improve the stability of Cu$_x$O photocathodes synthesized by the reduction of spin-coated CuI thin films.

3. CONCLUSIONS

The Cu$_x$O thin films were successfully synthesized by the reduction of copper iodide (CuI) thin films deposited by the spin coating method from CuI solution dissolved in an acetonitrile solvent. The experimental findings reveal that the Cu$_x$O thin film annealed at 350 °C has a larger grain size with a smooth surface and high carrier density. This synthesized Cu$_x$O exhibited a photocurrent density of −19.12 mA/cm$^2$ at −1 V versus RHE and ABPE of 7.06% with better reproducibility when applied as a photocathode in the solar water-splitting system. Therefore, this work reveals that Cu$_x$O thin films synthesized by spin coating and reduction of CuI thin films using the acetonitrile solvent route have huge potential as photocathodes for solar hydrogen production by water splitting.

4. EXPERIMENTAL DETAILS

4.1. Materials. Copper(I) iodide powder (CuI, 99.5%), acetonitrile (CH$_3$CN, 99.8%), sodium hydroxide pellets (NaOH, 97%), and ITO-coated glass slides (surface resistivity of 8–12 Ω/sq) were purchased from Sigma-Aldrich. All the chemicals were used as purchased without further purification.

4.2. Preparation of the Cu$_x$O Electrode. Figure 7 shows the preparation steps of the copper oxide photocathode. First, the CuI thin films were prepared on commercialized indium-doped tin oxide (ITO)-coated glass substrates from a copper iodide (CuI) solution of 30 mg/mL in acetonitrile following a recipe reported in previous work. The ITO-coated glass substrates were cleaned using an ultrasonic vibrator where acetone, isopropanol, and distilled water were used in sequence for cleaning before the deposition of the films. CuI thin films were deposited on the ITO glass substrates by spin coating at a speed of 2000 rpm for 30 s following a preannealing process at 150 °C for 10 min. The process was repeated five times to deposit thicker films. Then, the Cu$_x$O films were produced through dipping of the CuI thin films in aqueous sodium hydroxide (NaOH) solution (0.25 mol L$^{-1}$). The Cu$_x$O thin films were then rinsed in methanol and dried in air to eliminate the undesired surplus. Because thermal treatment is an essential factor in the one-step solution process for the phase transformation of copper oxide, the synthesized photocathodes were finally annealed at temperatures of 250, 300, and 350 °C for 1 h. The thicknesses of the Cu$_x$O thin films were in the range of 650–700 nm.

4.3. Characterization. Structural properties of the copper oxide thin films were investigated using XRD with Cu Ka radiation having wavelength 1.540598 Å using the EMMA X-ray diffractometer (GBC Corporation, Australia). The surface morphology of the films was observed using a scanning electron microscope from EVO 18, Carl Zeiss, UK. The elemental composition of the films was measured by EDX using a Team EDS system (EDAX, AMETEK, USA; beam voltage: 15 kV). The Bruker Dektak XTL thickness profiler was used to measure the thickness of the films. The optical properties of the films were investigated using UV–visible spectrophotometry using a T60 UV–visible spectrophotometer (PG Instruments) with 1 nm increment in wavelength. Capacitance–voltage (C–V) measurement was done using an impedance analyzer (model: Agilent 4192 A). All the films were characterized at room temperature (−27 °C) and a relative humidity of ∼50%.

4.4. PEC Measurement. The PEC performance of the synthesized Cu$_x$O photocathodes was explored under 1.5 AM (100 mW/cm$^2$) simulated sun illumination using a Solar Light 16S-Series 150–300 W UVB solar simulator. The measurement was carried out in a well-recognized three-electrode PEC system, where platinum (Pt) as the CE, saturated Ag/AgCl as the RE and Cu$_x$O photocathode as the WE having an active area of 1.5 cm$^2$ were immersed in a 0.025 M H$_2$SO$_4$ aqueous electrolyte solution. For all samples, current versus potential measurements were recorded at a scanning rate of 10 mV s$^{-1}$ using a Squidstat plus potentiostat from Admiral Instruments, USA. The Cu$_x$O photocathode was installed perpendicularly to the direction of light illumination and illuminated from the front side because such alignment is convenient to utilize the performance of the photoelectrode properly. The two-electrode system (Cu$_x$O as the WE and Pt as the CE) was used to evaluate the PEC performance of the Cu$_x$O photocathodes in terms of ABPE (%).

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Notes
The authors declare no competing financial interest.

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References
(1) Paracchino, A.; Laporte, V.; Sivula, K.; Grätzel, M.; Thimsen, E. Highly Active Oxide Photocathode for Photoelectrochemical Water Reduction. Nat. Mater. 2011, 10, 436–461.
(2) Hossen, M. F.; Ismail, A. B. M. Investigation on Fe2O3/Por-Si Photocatalyst for Low-Bias Water-Splitting. J. Mater. Sci.: Mater. Electron. 2018, 29, 15480–15485.
(3) Van De Krol, R.; Liang, Y.; Schoonman, J. Solar Hydrogen Production with Nanostructured Metal Oxides. J. Mater. Chem. 2008, 18, 2311–2320.
(4) Cho, I. S.; Lee, C. H.; Feng, Y.; Logar, M.; Rao, P. M.; Cai, L.; Kim, D. R.; Sinclair, R.; Zheng, X. Codoping Titanium Dioxide Nanowires with Tungsten and Carbon for Enhanced Photoelectrochemical Performance. Nat. Commun. 2013, 4, 1723–1728.
(5) Montoya, J. H.; Seitz, L. C.; Chakhranont, P.; Vojvodic, A.; Jaramillo, T. F.; Nørskov, J. K. Materials for Solar Fuels and Chemicals. Nat. Mater. 2016, 15, 70–81.
(6) Finegold, L.; Cude, J. L. Biological Sciences: One and Two-Dimensional Structure of Alpha-Helix and Beta-Sheet Forms of Poly(L-Alanine) Shown by Specific Heat Measurements at Low Temperatures (1.5-20 K). Nature 1972, 238, 38–40.
(7) Robel, I.; Subramanian, V.; Kuno, M.; Kamat, P. V. Quantum Dot Solar Cells. Harvesting Light Energy with CdSe Nanocrystals Molecularly Linked to Mesoscopic TiO2 Films. J. Am. Chem. Soc. 2006, 128, 2385–2393.
(8) Stergiopoulos, T.; Arabatzis, I. M.; Katsaros, G.; Falaras, P. Binary Polyethylene Oxide/Titania Solid-State Redox Electrolyte for Highly Efficient Nanocrystalline TiO2 Photovoltaic Cells. Nano Lett. 2002, 2, 1259–1261.
(9) Wang, G.; Ling, Y.; Lu, X.; Wang, H.; Qian, F.; Tong, Y.; Li, Y. Solar Driven Hydrogen Release from Urea and Human Urine. Energy Environ. Sci. 2012, 5, 8215–8219.
(10) Nunes, D.; Pimentel, A.; Santos, L.; Barquinha, P.; Fortunato, E.; Martins, R. Photocatalytic TiO2 Nanorod Spheres and Arrays Compatible with Flexible Applications. Catalysts 2017, 7, 60.
(11) Yang, X.; Wolcott, A.; Wang, G.; Sobo, A.; Fitzmorris, R. C.; Qian, F.; Zhang, J. Z.; Li, Y. Nitrogen-Doped ZnO Nanowire Arrays for Photoelectrochemical Water Splitting. Nano Lett. 2009, 9, 2331–2336.
(12) Fichou, D.; Pouliquen, J.; Kossanyi, J.; Jakani, M.; Campet, G.; Claverie, J. Extension of the Photoresponse of Semiconducting Zinc Oxide Electrodes by 3d-Impurities Absorbing in the Visible Region of the Solar Spectrum. J. Electroanal. Chem. 1985, 188, 167–187.
(13) Jakani, M.; Campet, G.; Claverie, J.; Fichou, D.; Pouliquen, J.; Kossanyi, J. Photocatalytic Properties of Zinc Oxide Doped with 3d Elements. J. Solid State Chem. 1985, 56, 269–277.
(14) Cao, L.; Yuan, J.; Chen, M.; Shangguan, W. Photocatalytic Energy Storage Ability of TiO2-WO3 Composite Prepared by Wet-Chemical Technique. J. Environ. Sci. 2010, 22, 454–459.
(15) Qin, D.-B.; Tao, C.-L.; Friesen, S. A.; Wang, T.-H.; Varghese, O. K.; Bao, N.-Z.; Yang, Z.-Y.; Mallouk, T. E.; Grimes, C. A. Dense Layers of Vertically Oriented WO3 Crystals as Anodes for Photoelectrochemical Water Oxidation. Chem. Commun. 2012, 48, 729–731.
(16) Qi, H.; Wolfe, J.; Wang, D.; Fan, H. J.; Fichou, D.; Chen, Z. Triple-Layered Nanostructured WO3 Photoanodes with Enhanced Photocurrent Generation and Superior Stability for Photoelectrochemical Solar Energy Conversion. Nanoscale 2014, 6, 13457–13462.
(17) Yang, L.; Yi, G.; Hou, Y.; Cheng, H.; Luo, X.; Pavlostathis, S. G.; Luo, S.; Wang, A. Building Electrode with Three-Dimensional Macroporous Interface from Biocompatible Polypryroly and Conductive Graphene Nanosheets to Achieve Highly Efficient Microbial Electrocatlysis. Biosens. Bioelectron. 2019, 141, 111444.
(18) Cesar, I.; Kay, A.; Gonzalez Martinez, J. A.; Grätzel, M. Translucent Thin Film Fe2O3 Photoanodes for Efficient Water Splitting by Sunlight: Nanostructure-Directing Effect of Si-Doping. J. Am. Chem. Soc. 2006, 128, 4582–4583.
(19) Luo, W.; Yang, Z.; Li, Z.; Zhang, J.; Liu, J.; Zhao, Z.; Wang, Z.; Yan, S.; Yu, T.; Zou, Z. Solar Hydrogen Generation from Seawater with a Modified BiVO4 Photocathode. Energy Environ. Sci. 2011, 4, 4046–4051.
(20) McShane, C. M.; Choi, K.-S. Photocurrent Enhancement of N-Type Cu2O Electrodes Achieved by Controlling Dendritic Branching Growth. J. Am. Chem. Soc. 2009, 131, 2561–2569.
(21) Minguex-Bacho, I.; Courté, M.; Fan, H. J.; Fichou, D. Conformal Cu3S-Coated Cu2O Nanostuctures Generated by Ion Exchange Reaction and Their Photocatalytic Properties. Nanotechnology 2015, 26, 185401.
(22) Kang, Z.; Yan, X.; Wang, Y.; Bai, Z.; Liu, Y.; Zhang, Z.; Lin, P.; Zhang, X.; Yuan, H.; Zhang, X.; Zhang, Y. Electronic Structure Engineering of Cu2O Film/ZnO Nanorods Array All-Oxide p-n Heterostructure for Enhanced Photocatalytic Hydrogen Production. Applied Catalysis B: Environmental 2018, 232, 58. 124–129.
(23) Zhang, H.; Cao, J.-L.; Shao, G.-S.; Yuan, Z.-Y. Synthesis of Cu2O Photocathode for Low Bias Photoelectrochemical Water Splitting Enabled by NiFe-Layered Double Hydroxide Co-Catalyst. Sci. Rep. 2016, 6, 30882.
(24) Lim, Y.-F.; Chua, C. S.; Lee, C. J. J.; Chu, D. Sol-Gel Deposition Cu2O and CuO Thin Films for Photocatalytic Water Splitting. Phys. Chem. Chem. Phys. 2014, 16, 25928–25934.
(25) Nunes, D.; Pimentel, A.; Gonçalves, A.; Pereira, S.; Branquinho, R.; Barquinha, P.; Fortunato, E. Metal Oxide Nanostuctures for Sensor Applications. Sensicon. Sci. Technol. 2019, 34, 03001.
(26) Martin, V.; Gonçalves, V.; Rodríguez-Rojro, S.; Nunes, D.; Fortunato, E.; Martins, R.; Cosco, M. J. Duarte, C. Production of Copper Loaded Lipid Microparticles by PGSS® (Particles from Gas Saturated Solutions) Process. J. Supercrit. Fluids 2018, 131, 124–129.
(27) Zhang, H.; Cao, J.-L.; Shao, G.-S.; Yuan, Z.-Y. Synthesis of Transition Metal Oxide Nanoparticles with Ultrahigh Adsorption Capacity and Efficient Catalytic Oxidation Performance. J. Mater. Chem. 2009, 19, 6097–6099.
(28) Masudy-Panah, S.; Siavash Moakhar, R.; Chua, C. S.; Kushwaha, A.; Dalapati, G. K. Stable and Efficient CuO Based Photocathode through Oxygen-Rich Composition in Au-Pd Nanostucture Incorporation for Solar-Hydrogen Production. ACS Appl. Mater. Interfaces 2017, 9, 27596–27606.
(29) John, S.; Roy, S. C. Cu2O/CuO Nanofoil/Nanowire Heterostructure Photocathode with Enhanced Surface Area for Photoelectrochemical Solar Energy Conversion. Appl. Surf. Sci. 2020, 509, 144703.
(30) Chiang, C.-Y.; Shin, Y.; Aroh, K.; Ehrman, S. Copper Oxide Photocathodes Prepared by a Solution Based Process. Int. J. Hydrogen Energy 2012, 37, 8232–8239.
(31) Baran, T.; Wojtyła, 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.

(32) Liu, A.; Nie, S.; Liu, G.; Zhu, H.; Zhu, C.; Shin, B.; Fortunato, E.; Martins, R.; Shan, F. In Situ One-Step Synthesis of p-Type Copper Oxide for Low-Temperature, Solution-Process Thin-Film Transistors. J. Mater. Chem. C 2017, 5, 2524−2530.

(33) Patel, M.; Pali, R.; Marathey, P.; Kim, J.; Mukhopadhyay, I.; Ray, A. Highly Photoactive and Photo-Stable Pyrolyzed Tenorite CuO Thin Films for Photocatalytic Energy Conversion. J. Electrochem. Soc. 2016, 163, H1195−H1203.

(34) Yang, Y.; Xu, D.; Wu, Q.; Diao, P. CuO/CuO Bilayered Composite as a High-Efficiency Photocathode for Photocatalytical Hydrogen Evolution Reaction. Sci. Rep. 2016, 6, 35158.

(35) Jung, K.; Lim, T.; Bae, H.; Ha, J. S.; Martinez-Morales, A. A. CuO Photocathode with Faster Charge Transfer by Fully Reacted Cu Seed Layer to Enhance Performance of Hydrogen Evolution in Solar Water Splitting Applications. ChemCatChem 2019, 11, 4377−4382.

(36) Cao, D.; Nasori, N.; Wang, Z.; Wen, L.; Xu, R.; Mi, Y.; Lei, Y. Facile Surface Treatment on CuO Photocathodes for Enhancing the Photoelectrochemical Response. Appl. Catal., B 2018, 198, 398−403.

(37) Son, M.-K.; Steier, L.; Schreier, M.; Mayer, M. T.; Lu, J.; Grätzel, M. A Copper Nickel Mixed Oxide Hole Selective Layer for Au-Free Transparent Cuprous Oxide Photocathodes. Energy Environ. Sci. 2017, 10, 912−918.

(38) Shinde, P. S.; Fontenet, P. R.; Donahue, J. P.; Waters, J. L.; Kung, P.; McNamara, L. E.; Hammer, N. I.; Gupta, A.; Pan, S. Synthesis of MoS2 from [MoO3(S2CNEt2)2] for Enhancing Photoelectrochemical Performance and Stability of Cu2O Photocathode toward Efficient Solar Water Splitting. J. Mater. Chem. A 2018, 6, 9569−9582.

(39) Azevedo, J.; Steier, L.; Dias, P.; Stelik, M.; Sousa, C. T.; Araújo, J. P.; Mendes, A.; Graetzel, M.; Tilley, S. D. On the Stability Enhancement of Cuprous Oxide Water Splitting Photocathodes by Low Temperature Steam Annealing. Energy Environ. Sci. 2014, 7, 4044−4052.

(40) Morales-Guio, C. G.; Tilley, S. D.; Vrbel, H.; Graetzel, M.; Hu, X. Hydrogen Evolution from a Copper(I) Oxide Photocathode Coated with an Amorphous Molybdenum Sulphide Catalyst. Nat. Commun. 2014, 5, 3059.

(41) Zhang, L.; Jing, D.; Guo, L.; Yao, X. In Situ Photochemical Synthesis of Zn-Doped CuO Hollow Microcubes for High Efficient Photocatalytic H2 Production. ACS Sustainable Chem. Eng. 2014, 2, 1446−1452.

(42) Hsu, Y.-K.; Yu, C.-H.; Chen, Y.-C.; Lin, Y.-G. Synthesis of Novel CuO:Si Micro/Nanostructured Photocathode for Solar Water Splitting. Electrochim. Acta 2013, 105, 62−68.

(43) Zoó, C.; Ding, L. Solution-Processed Cu2O and CuO as Hole Transport Materials for Efficient Perovskite Solar Cells. Small 2015, 11, 5528−5532.

(44) Rahman, M.; Newaz, M. A.; Mondal, B. K.; Kuddus, A.; Karim, M. A.; Rashid, M. M.; Rubel, M. H. K.; Hossain, J. Unraveling the Electrical Properties of Solution-Processed Copper Iodide Thin Films for CSp/n-Si Solar Cells. Mater. Res. Bull. 2019, 118, 110518.

(45) De Los Santos Valladares, L.; Salinas, D. H.; Dominguez, A. B.; Najarro, D. A.; Khondaker, S. I.; Mitrelas, T.; Barnes, C. H. W.; Aguilar, J. A.; Majima, Y. Crystallization and Electrical Resistivity of Cu2O and CuO Obtained by thermal Oxidation of Cu Thin Films on SiO2/Si Substrates. Thin Solid Films 2012, 520, 6368−6374.

(46) Tamaekong, N.; Liewhuran, C.; Phanchaphant, S. Synthesis of Thermally Spherical CuO Nanoparticles. J. Nanomater. 2014, 2014, 509798.

(47) Ahmad, A. A.; Aissa, A. M.; Al-Bataineh, Q. M.; Al-Akhras, M. A. H.; Albataine, Z.; Alizy, K. A.; Daoud, N. S. Synthesis and Characterization of ZnO NPs-Doped PMMA-BDK-MR Polymer-Coated Thin Films with UV Curing for Optical Data Storage Applications. Polym. Bull. 2020, DOI: 10.1007/s00289-020-03155-x.
(66) 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.

(67) Masudy-Panah, S.; Siavash Moakhar, R.; Chua, C. S.; Tan, H. R.; Wong, T. I.; Chi, D.; Dalapati, G. K. Nanocrystal Engineering of Sputter-Grown CuO Photocathode for Visible-Light-Driven Electrochemical Water Splitting. ACS Appl. Mater. Interfaces 2016, 8, 1206–1213.

(68) 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.

(69) Dalapati, G. K.; Masudy-Panah, S.; Moakhar, R. S.; Chakrabortty, S.; Ghosh, S.; Kushwaha, A.; Katal, R.; Chua, C. S.; Xiao, G.; Tripathy, S.; Ramakrishna, S. Nanoengineered Advanced Materials for Enabling Hydrogen Economy: Functionalized Graphene—Incorporated Cupric Oxide Catalyst for Efficient Solar Hydrogen Production. Global Challenges 2020, 4, 1900087.

(70) 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.

(71) Toe, C. Y.; Zheng, Z.; Wu, H.; Scott, J.; Amal, R.; Ng, Y. H. Photocorrosion of Cuprous Oxide in Hydrogen Production: Ration-alisng Self-Oxidation or Self-Reduction. Angew. Chem., Int. Ed. 2018, 57, 13613–13617.