Highly stable copper oxide composite as an effective photocathode for water splitting via a facile electrochemical synthesis strategy†

Zhonghai Zhangab and Peng Wang*ab

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Hydrogen generation through photoelectrochemical (PEC) water splitting using solar light as an energy resource is believed to be a clean and efficient way to overcome the global energy and environmental problems. Extensive research effort has been focused on n-type metal oxide semiconductors as photoanodes, whereas studies of p-type metal oxide semiconductors as photocathodes where hydrogen is generated are scarce. In this paper, highly efficient and stable copper oxide composite photocathode materials were successfully fabricated by a facile two-step electrochemical strategy, which consists of electrodeposition of a Cu film on an ITO glass substrate followed by anodization of the Cu film under a suitable current density and then calcination to form a Cu2O/CuO composite. The synthesized Cu2O/CuO composite was composed of a thin layer of Cu2O with a thin film of CuO on its top as a protecting coating. The rational control of chemical composition and crystalline orientation of the composite materials was easily achieved by varying the electrochemical parameters, including electrodeposition potential and anodization current density, to achieve an enhanced PEC performance. The best photocathode material among all materials prepared was the Cu2O/CuO composite with Cu2O in (220) orientation, which showed a highly stable photocurrent of −1.54 mA cm−2 at a potential of 0 V vs reversible hydrogen electrode at a mild pH under illumination of AM 1.5G. This photocurrent density was more than 2 times that generated by the bare Cu2O electrode (−0.65 mA cm−2) and the stability was considerably enhanced to 74.4% from 30.1% on the bare Cu2O electrode. The results of this study showed that the top layer of CuO in the Cu2O/CuO composite not only minimized the Cu2O photocorrosion but also served as a recombination inhibitor for the photogenerated electrons and holes from Cu2O, which collectively explained much enhanced stability and PEC activity of the Cu2O/CuO composite. Thus, the electrochemical strategy proposed in this study for the synthesis of the Cu2O/CuO composite opens a new way to use copper oxides as photocathode materials in PEC cells for a highly stable and effective water splitting.

1. Introduction

Highly effective utilization of solar energy is arguably the most promising way to address the issues of energy shortage, climate change, and environmental pollution. Solar energy collection, conversion and storage are three key processes for practical applications and these processes can all be integrated in a single monolithic photoelectrochemical (PEC) water splitting cell, within which the solar energy is converted and contained in the simplest chemical bond, H–H, as hydrogen gas.1–3 Hydrogen, due to its high mass energy density and its environmental friendliness, is undeniably one of the most promising fuels as motive power. Therefore, efficient water splitting into usable hydrogen by PEC cells driven by solar energy has inspired tremendous research efforts in both academia and industry.4–8

Within a PEC cell, under solar light illumination, photogenerated electrons and holes on semiconductor electrode materials (i.e., electrons from p-type semiconductors and/or holes from n-type semiconductors) are driven into a solution by the electric field present on the semiconductor/liquid junction to induce water redox reactions, including reduction of H+ to H2 and oxidation of OH− to O2.9–12 Thus, n-type semiconductors are suitable as photoanode materials while p-type semiconductors are for photocathode materials. Ideally, PEC water splitting requires electrode materials that have: (1) a proper band gap (∼1.6–2.2 eV); (2) band edge alignment that straddles the H2 and O2 reaction potentials; (3) high energy conversion efficiency; (4) stability in the operating
environment; and (5) low production cost and an abundant natural source which is desirable for large-scale applications.

Since the pioneering work of photoelectrolysis on n-type TiO$_2$ electrodes by Fujishima and Honda in 1972, a lot of n-type metal oxide semiconductors, such as TiO$_2$, ZnO, Fe$_2$O$_3$, WO$_3$, and Cu$_2$O have been extensively studied as potential photoanode materials in PEC processes. In a sharp contrast, research effort in photocathode materials has been disproportionately little. Up to now, there have been just few reports published on n-type semiconductor based photocathode materials, among which copper oxide distinguishes itself due to its high photoactivity, natural abundance of copper, and its low-cost production. Copper oxide is known to exist in two semiconducting phases, namely, cupric oxide (CuO) and cuprous oxide (Cu$_2$O). As compared with CuO, Cu$_2$O receives considerably more research attention as a photocathode, due to its direct band gap of 2 eV which is suitable for solar energy harvesting, a corresponding theoretical photocurrent of $-14.7$ mA cm$^{-2}$, a suitable conduction band position (0.7 V negative of the hydrogen generation potential) which is suitable for hydrogen generation, and a high light-to-hydrogen conversion efficiency of 18.7% based on the AM 1.5 spectrum.

Various synthesis methods have been explored for preparation of highly photoactive Cu$_2$O, such as sputtering, thermal evaporation, sonochemical, thermal relaxation, seed mediated synthesis method, holographic lithography, and electrochemical synthesis. Among these methods, electrochemical synthesis is favored by many due to its flexibility, relatively low-cost, and the ease with which the morphology, structure, and orientation of the final products can be controlled. However, the main barrier to overcome for the use of Cu$_2$O as an efficient photocathode in a practical PEC cell is its poor stability in aqueous solution under illumination, which holds back the progress in this field. In a very recent publication, Grätzel and Thimsen et al. (2011) employed an atomic layer deposition method and successfully formed an ultrathin Al/ZnO/TiO$_2$ coating on Cu$_2$O surface as a protective layer, which significantly increased Cu$_2$O stability. However, the inherent complexity of the material fabrication processes in this case limits its possibility of scaling up. Thus, alternative methods are still much needed for the synthesis of a low-cost, highly stable and effective Cu$_2$O photocathode for PEC water splitting applications.

In this paper, for the first time, a facile electrochemical strategy is proposed and successfully employed for preparation of a copper oxide composite photocathode (Cu$_2$O/CuO), which consisted of a thin layer of Cu$_2$O with a layer of CuO coating atop. CuO is a very stable phase of copper oxide and thus was used as a protection layer to keep Cu$_2$O from photo-corrosion. The Cu$_2$O/CuO composite was synthesized directly from a Cu film substrate on top of an ITO glass by a rational selection of anodization current density. A high and stable PEC activity of the Cu$_2$O/CuO composite as a photocathode for hydrogen generation was confirmed.

2. Experimental

2.1. Electrochemical preparation of copper oxide

All of the chemical reagents used in the study were of analytical grade and were used without further purification. The copper oxide composite photoelectrode was fabricated by a two-step electrochemical process. In the first step, a copper film was electrodeposited on the ITO surface from a Cu(NO$_3$)$_2$ solution with a different potential of $-0.6$, $-0.8$ and $-1.0$ V at the same deposition time of 10 min. In the second step, the deposited Cu films were anodized in an alkaline solution (3 M NaOH) for 30 min under different current densities: 1.5, 3.0, and 5.0 mA cm$^{-2}$, separately and different chemical compositions obtained on the Cu films under different anodization current densities were Cu$_2$O, Cu$_2$O/Cu(OH)$_2$, and Cu(OH)$_2$, respectively. The typical electrochemical curves of electrodeposition and anodization can be found in Fig. S1.† The temperature of the electrochemical cells was maintained at 25 °C for all experiments. The as-anodized Cu$_2$O/Cu(OH)$_2$ composite was calcined at 400 °C for 1 h in ambient conditions to get Cu$_2$O/CuO composite.

2.2. Structural characterization

The morphology of the prepared copper oxide photoelectrodes was characterized by scanning electron microscopy (SEM, FEI, Quanta 600). The chemical compositions were determined by energy dispersive spectrometer (EDS) equipped with FESEM. The crystalline structure was analyzed by X-ray diffraction (XRD) (Bruker D8 Discover diffractometer, using Cu K$_\alpha$ radiation, 1.540598 Å). X-ray photoelectron spectroscopy (XPS) data were collected by an Axis Ultra instrument (Kratos Analytical) under ultrahigh vacuum (<$10^{-8}$ Torr) and by using a monochromatic Al K$_\alpha$ X-ray source. The adventitious carbon 1s peak was calibrated at 285 eV and used as an internal standard to compensate for any charging effects. The UV-vis adsorption spectra were recorded on spectrophotometer ( Beckman Coulter, Du80).

2.3. Photoelectrochemical measurements

The PEC performance of the prepared copper oxide photoelectrodes was evaluated using a three-electrode configuration with copper oxide photoelectrodes, Ag/AgCl electrode, and Pt mesh as working electrodes, reference electrode, and counter electrode, respectively. The electrolyte used was 50 mM Na$_2$SO$_4$ solution buffered at pH 6.82. The photoresponse of the prepared photoelectrodes was measured under chopped irradiation from a 300 W Xe lamp (PLS-SXE300) equipped with ultraviolet and infrared filters. The intensity of the light source was calibrated with a Si diode (Newport) to simulate AM 1.5 illumination (100 mW cm$^{-2}$). The scan rate for the linear sweep voltammetry was 5 mV s$^{-1}$. The PEC stability of the materials was evaluated by measuring the photocurrent densities produced under chopped light irradiation (light on/off cycles: 10 s) at a fixed electrode potential of 0 V vs RHE. The impedance measurements were performed using a PGSTAT302N Autolab Potentiostat/Galvanostat (Metrohm) equipped with a frequency analyzer module (FRA2). The electrochemical impedance spectra (EIS) were done at an excitation signal of 10 mV amplitude. The impedance vs frequency spectra were acquired at fixed sample potentials. Afterwards, impedance vs potential measurement at fixed frequencies was performed.

3. Results and discussion

Fig. 1 presents a measured cyclic voltammogram (CV) of a bare ITO electrode in 1 mM Cu(NO$_3$)$_2$ solution, which shows
important information about oxidation state changes of copper as a function of the applied potentials. The CV was obtained by sweeping from positive to negative potentials (cathodic sweep) with a slow potential scan rate of 5 mV s\(^{-1}\), followed by the same scan rate but in a reverse direction (anodic sweep). The first cathodic peak at \(-0.075\) V is associated with Cu(II) to Cu(I) reduction, and the second cathodic peak at \(-0.400\) V is with a further reduction of Cu(I) to Cu(0). The anodic peaks observed at \(-0.240\) and 0.089 V (accompanied by a satellite peak at 0.032 V) correspond to Cu(0) to Cu(I) and Cu(I) to Cu(II) oxidation, respectively. The above information guides the controlled synthesis of the copper oxide composite photocathode throughout.

Scheme 1 presents the electrochemical synthesis strategy of the copper oxide composite photocathode. In more detail, an ITO glass is first used as an electrode onto which a thin film of copper metal is deposited via electroreduction of Cu\(^{2+}\) \rightarrow Cu(s) at proper negative potentials of \(-0.6\), \(-0.8\), and \(-1.0\) V, (vs Ag/AgCl) separately. The deposited Cu film not only serves as a precursor for subsequent synthesis of copper oxides, but also enhances the electronic conductivity of the electrode. The Cu film then undergoes anodization in an alkali medium (pH \(= 14.56\) by 3 M NaOH) to form Cu\(_2\)O or Cu(OH)\(_2\) on its top. It is known that during anodization the oxidation states of copper oxide, Cu\(_2\)O and Cu(OH)\(_2\), can be tuned by applied current density. At a low electric current density, the Cu is oxidized to Cu\(^{+}\), which is in turn combined with OH\(^-\) ions to form Cu\(_2\)O. The Cu\(_2\)O self-assembles to form a Cu\(_2\)O nanostructure on the surface of the Cu film. At high current density which renders an increased anodization level, a high copper valence: Cu\(^{2+}\), is obtained, in the form of Cu(OH)\(_2\) nanostructure on top of the Cu film. This result implies that the orientations of Cu\(_2\)O can be tuned by adjusting the preferred orientations of this material. Specifically, for Cu-1.0 shows an almost single orientation of (220) and the preferred orientation in Cu-0.8 is also (220), although some other diffraction peaks of (111) and (200) can be observed. The Cu-0.6 sample shows a totally different preferred orientation of (111) direction. The differences in the orientations of the Cu films may influence the growth directions of the overlying Cu\(_2\)O, which in turn may affect the performance of the photocathodes thus prepared.

Fig. 3 shows typical SEM images of the Cu/Cu\(_2\)O materials prepared by anodization at a constant current density of 1.5 mA cm\(^{-2}\) for 30 min on different Cu films. All samples show similar polyhedral structures (Fig. 3a, b and c). The XRD patterns in Fig. 3d show that all samples were anodized to Cu\(_2\)O solely on the Cu films and there was no Cu(II) species detected. It was also found that the Cu\(_2\)O formed on Cu-1.0 and Cu-0.8 showed a preferred orientation of (220) direction whereas that on Cu-0.6 showed a preferred orientation of Cu\(_2\)O (111), which are the same preferred orientations as those of the underlying Cu films. This result implies that the orientations of the Cu\(_2\)O can be adjusted by controlling the orientations of the Cu films.

Fig. 4 shows typical SEM images of Cu(OH)\(_2\) nanostructures on the Cu films prepared at a constant current density of 5 mA cm\(^{-2}\) for 30 min, under which no Cu\(_2\)O was formed and Cu(OH)\(_2\) was the only anodization product. Interestingly, it can be found that the Cu(OH)\(_2\) formed on Cu-1.0 shows a unique nanonet structure (Fig. 4a) and the high-magnification view in the inset shows that nanonet consists of lots of nanowires, just like a real bird’s net. Presumably, the nanowires were formed from the bases of the special fish scale structures on the Cu-1.0 surface (Fig. 2a). On the other hand, the Cu(OH)\(_2\) formed on Cu-0.8 surface shows a randomly packed nanorod structure (Fig. 4b). A nanoflower structure of Cu(OH)\(_2\) was formed on Cu-0.6 surface and each nanoflower was composed of lots of assembled nanorods (Fig. 4c). Fig. 4d shows the XRD patterns of as-prepared Cu/Cu(OH)\(_2\) (the peaks marked with stars are the diffraction lines of the Cu film). The diffraction peaks at 23.8° and 34.2° of Cu(OH)\(_2\) can be indexed to spertiniite with orientations of (021) and (002) respectively. The absence of diffraction peaks of Cu\(_2\)O and CuO in the XRD patterns confirms the formation of pure Cu(OH)\(_2\) on the Cu films.

As shown above, Cu\(_2\)O and Cu(OH)\(_2\) can be synthesized from the same Cu film substrate under different anodization current densities, so it is thus hypothesized that the synthesis of
a Cu2O/Cu(OH)2 composite, namely, a Cu2O layer coated with a Cu(OH)2 film, can be obtained by a rational selection of a suitable anodization current density.

Based on the hypothesis and on the previous results, a moderate current density of 3 mA cm−2 was selected and applied in the anodization process and the desired composite materials were successfully prepared. Fig. 5 shows SEM images of the Cu2O/Cu(OH)2 composite films and the corresponding XRD patterns. In terms of surface morphology, similar nano-flower structures are clearly found on the entire surface of the Cu2O/Cu(OH)2 composite film prepared from Cu-1.0 (Fig. 5a, 5a-1, 5a-2) while the composite films formed on Cu-0.8 (Fig. 5b) and Cu-0.6 (Fig. 5c) show nanorod structures and there is no clear nanoflower pattern visible on their surfaces. The EDS analysis of the Cu-1.0/Cu2O/Cu(OH)2 sample indicates the existence of both Cu and O elements (Fig. S2b)† and the SEM image of the same sample presents a cross-sectional view, which clearly shows the boundaries of different copper layers (Fig. S3).‡ All XRD patterns show coexistence of Cu2O and Cu(OH)2, which supports the hypothesis. The Cu-1.0/Cu2O/Cu(OH)2 sample still shows a strong Cu2O (220) orientation, which implies that the primary orientations of the prepared Cu2O/Cu(OH)2 composite materials significantly depend on these of the Cu film substrates in the anodization processes.

It is now clear that a low anodization current density favors the formation of Cu2O, a high current density is advantageous for the formation of Cu(OH)2, and a moderate current density in between causes the co-existence of different oxidation states, Cu2O/Cu(OH)2. Based on these, the formation mechanism of the Cu2O/Cu(OH)2 composite is postulated as follows. At a high current density: Cu + 2e− → Cu2+, Cu2+ + 2OH− → Cu(OH)2↓; at a low current density: Cu + e− → Cu+, 2Cu2+ + 2OH− → Cu2O↓ + H2O; and at a moderate current density, both kinds of reactions occur. It is known that the formation of a high copper oxidation state is more favorable at a solid/liquid interface where electrochemical anodization is always more powerful than a bulk phase,39 so the formation of Cu(OH)2 on the top surface and the formation of Cu2O in the underlying bulk phase are more favorable. In addition, the Cu film at the bottom discourages the...
formation of a high oxidation state copper oxide (CuO) as its neighboring layer and thus only permits the formation of Cu₂O on its top.

The prepared Cu/Cu₂O/Cu(OH)₂ samples were calcined at 400 °C for 1 h in ambient air to dehydrate and crystallize for obtaining Cu₂O/CuO, during which most of the Cu film substrate was oxidized to Cu₂O. Fig. 6 presents the SEM images and XRD patterns of the prepared Cu₁₀/Cu₂O/Cu(OH)₂ samples. Clearly, the surface nanoflower patterns remain after calcination. The XRD patterns confirm a complete conversion of Cu(OH)₂ to CuO and a high level of Cu oxidation to Cu₂O, as indicated by an absence of Cu(OH)₂ peaks and much diminished Cu peaks, respectively (Fig. 6c).

The XPS spectra of the Cu₂O/Cu(OH)₂ composite is presented in Fig. 7, which is corrected with reference to C 1s peak at 285 eV (Fig. 7b). The full survey (Fig. 7a) indicates the presence of Cu and O and no obvious impurities could be found on the surface of the Cu₂O/Cu(OH)₂ composite. The XPS of Cu 2p core level is presented in Fig. 7c. The two peaks located at around 934.4 and 954.0 eV are assigned to the binding energy of Cu 2p₃/2 and Cu 2p₁/2, respectively, indicating the presence of the Cu²⁺ on the sample. Moreover, the two extra shake-up satellite peaks are also observed on a higher binding energy side, 942.0 and 962.2 eV for Cu 2p₃/2 and Cu 2p₁/2, respectively, implying the presence of an unfilled Cu 3d⁹ shell and thus further confirming the existence of Cu²⁺ on the sample surface. From the peak-fit for the Cu 2p, we find two other small peaks with binding energy of 932.6 and 952.6 eV, which are assigned to Cu 2p₃/2 and Cu 2p₁/2 in Cu₂O, respectively. The strong XPS peaks of Cu²⁺ and relatively low peaks for Cu⁺ imply a dense protection layer of Cu(OH)₂ on top of Cu₂O. Fig. 7d presents the O 1s core level XPS by using two Gaussian peaks, after Shirley background subtraction. The broad and asymmetric nature of the peak can be ascribed to multiple co-ordinations of oxygen in the nanostructure. The deconvoluted peaks at a binding energy of 530.8 and 531.1 eV are attributed to oxygen in Cu(OH)₂ and Cu₂O, respectively.

To evaluate the PEC water splitting activity of various materials prepared earlier as photocathodes, linear sweep photovoltammetry was used under 0.2 Hz chopped illumination with an intensity of 100 mW cm⁻² in 50 mM Na₂SO₄ buffered at a pH of 6.82, which was the electrolyte used in all PEC experiments in this study. The photovoltammetry of the different photocathode materials is presented in Fig. 8, which is used to evaluate the materials’ electrochemical behavior in the dark and their PEC activities under illumination under the same experimental conditions. The Cu₁₀/Cu₂O/Cu(OH)₂ composite electrode showed a photocurrent density of ~1.28 mA cm⁻² (Fig. 8c) at 0 V vs reversible hydrogen electrode (RHE), much higher than ~0.65 mA cm⁻² on the Cu₁₀/Cu₂O electrode (Fig. 8a) and ~0.37 mA cm⁻² on the Cu₁₀/Cu(OH)₂ electrode (Fig. 8b). This result suggests that the composite is beneficial for an enhanced PCE activity of the electrode. The enhanced PEC activities are due to the fact that the band edge potentials of Cu₂O and Cu(OH)₂ make a suitable band energy offset, which is advantageous for
electron flow, and thus for reducing the recombination of electrons and holes. Not surprisingly, the Cu-1.0/Cu_2O/CuO composite electrode showed the highest photocurrent density of $1.54 \text{ mA cm}^{-2}$ (Fig. 8d) among all the materials. A higher photocurrent density of Cu-1.0/Cu_2O/Cu(OH)_2 than Cu-1.0/Cu_2O/Cu(OH) can be attributed to its higher crystalline structure. The PEC activities of Cu-0.8/Cu_2O/Cu(OH)_2 and Cu-0.6/Cu_2O/Cu(OH)_2 electrodes were also studied (Fig. 8e and f) and pretty low photocurrent densities were observed on these electrodes, 0.41 and 0.031 mA cm$^{-2}$ for Cu-0.8/Cu_2O/CuO and Cu-0.6/Cu_2O/CuO, respectively. As compared to the high photocurrent density of $1.28 \text{ mA cm}^{-2}$ for Cu-1.0/Cu_2O/Cu(OH)_2, the low photocurrent densities of Cu-0.8/Cu_2O/Cu(OH)_2 and Cu-0.6/Cu_2O/Cu(OH)_2 very much stress a critical role of the preferred orientations of Cu_2O within the composite materials to the materials’ overall PEC. The Cu_2O with (220) orientation showed a significantly better PEC performance than others. Higher electron mobility in some preferred crystal orientations has been reported in a lot of studies for Fe_2O_3, TiO_2, and ZnO, so we suspect that the electron mobility in (220) direction of Cu_2O is significantly higher than in other directions. Experiments are currently being conducted to test this hypothesis. Therefore, a preferred crystal orientation and a high crystalline degree are beneficial for PEC activity enhancement of copper oxide composite photocathodes. Means of further increasing the composite material crystalline degree while keeping its preferred (220) orientation are currently under investigation in our group.

As to the material stability under illumination, the insets in Fig. 8 show photocurrent stability measurements on different materials held at 0 V vs RHE under chopped illumination with a frequency of 0.1 Hz. The Cu/Cu_2O electrode showed the poorest stability among all, with 70% decay of the photocurrent in 20 min (Fig. 8a). Although the Cu-1.0/Cu(OH)_2 electrode generated very poor photocurrent density ($0.37 \text{ mA cm}^{-2}$), it showed high stability as expected, with more than 80% photocurrent density remaining after 20 minutes illumination. With Cu(OH)_2 or CuO on the surface of Cu_2O as a protection layer, the Cu-1.0/Cu_2O/Cu(OH)_2 and Cu-1.0/Cu_2O/CuO composite photoelectrodes showed both high stability and high photocurrent density. The Cu-0.8/Cu_2O/Cu(OH)_2 and Cu-0.6/Cu_2O/Cu(OH)_2 photoelectrodes showed good stability in aqueous solution (Fig. 8e and f), although very low photocurrent densities. All
measured photocurrent densities and stabilities of these electrode materials are summarized in Table 1 and these results together confirm that a more stable copper species: Cu(OH)₂ or CuO, (1) provides an excellent protection against Cu₂O photocorrosion and (2) serves as a recombination inhibitor for photogenerated electrons and holes from Cu₂O and thus enhances the photocurrent density.

Electrochemical impedance spectroscopy (EIS) is a powerful tool for studying materials’ PEC properties. The EIS measurement was carried out covering a frequency of 10⁵–0.1 Hz intervals using an amplitude of 10 mV at a bias potential of −0.24 V. Fig. 9 presents Nyquist plots for various copper oxide electrodes, Cu-1.0/Cu(OH)₂, Cu-1.0/Cu₂O, Cu-1.0/Cu₂O/Cu(OH)₂, and Cu-1.0/Cu₂O/CuO, both in the dark and under illumination. It is known that the semicircle in a Nyquist plot at high frequencies is characteristic of the charge transfer process and the diameter of the semicircle is equal to the charge transfer resistance (Rct). Thus, the Rct under illumination is lower than the Rct in the dark on all the photoelectrode materials, which may be due to an increased electron conductivity of the photocathodes under illumination. The Cu-1.0/Cu₂O/CuO showed a lower Rct value and higher conductivity than other materials both in the dark and under illumination, which partially explains its better PEC performance as shown earlier.

The capacitance measurement on the electrode/electrolyte was also employed to determine the flat band (Ufb) and carrier density (Nₐ), which can be obtained in a Mott-Schottky (MS) plot with 1/C² vs. potential at a fixed frequency of 1kHz. The capacitance-potential measurements on Cu-1.0/Cu₂O/CuO electrode are presented as a MS plot following the equation below:

\[
\frac{1}{C^2} = \frac{2}{N_\text{a} \varepsilon_0 \varepsilon} \left[ (U_s - U_{\text{FB}}) - \frac{kT}{e} \right]
\]

where C is the space charge capacitance in the semiconductor; Nₐ is the hole carrier density; e is the elemental charge value; ε₀ is the permittivity of the vacuum; ε is the relative permittivity of the semiconductor (ε of Cu₂O is 7.60 and that of CuO is 10.26); Uₛ is the applied potential, T is temperature, and k is the Boltzmann constant. The MS plot is presented in Fig. 10 as 1/C² vs potential. The slope of the linear part of the curve in the MS plot is negative, indicating a p-type semiconductor. The linear part of the curve is extrapolated to 1/C² = 0, and the value of V_FH is estimated to be 0.67 V vs RHE. The Nₐ of Cu-1.0/Cu₂O/CuO is calculated from the slope to be 2.08 × 10¹⁹ cm⁻³, which is significantly higher than the previously reported data on single phase Cu₂O films (6.12 × 10¹⁷~1.36 × 10¹⁸). A higher Nₐ also suggests a higher density of the vacancies with Cu-1.0/Cu₂O/CuO, implying a faster carrier transfer rate and thus an enhanced PEC performance.

A tentative energy diagram of Cu/Cu₂O/CuO photocathode is depicted in Scheme 2. A typically staggered type II band energy offset between Cu₂O and Cu is suggested. It is known that Cu₂O is a direct band gap semiconductor while CuO is an indirect band gap semiconductor. Therefore, the tendency of the valence electrons in bare Cu₂O to be excited by illumination as

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Table 1: Summary of PEC performance of different composite photocathodes

<table>
<thead>
<tr>
<th>Samples</th>
<th>Photocurrent density at 0 V vs RHE [mA cm⁻²]</th>
<th>Stability after 20 min illumination</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu-1.0/Cu₂O</td>
<td>−0.65</td>
<td>30.1%</td>
</tr>
<tr>
<td>Cu-1.0/Cu(OH)₂</td>
<td>−0.37</td>
<td>80.7%</td>
</tr>
<tr>
<td>Cu-1.0/Cu₂O/Cu(OH)₂</td>
<td>−1.28</td>
<td>85.8%</td>
</tr>
<tr>
<td>Cu-1.0/Cu₂O/CuO</td>
<td>−1.54</td>
<td>74.4%</td>
</tr>
<tr>
<td>Cu-0.8/Cu₂O/CuO</td>
<td>−0.41</td>
<td>57.5%</td>
</tr>
<tr>
<td>Cu-0.6/Cu₂O/CuO</td>
<td>−0.031</td>
<td>61.4%</td>
</tr>
</tbody>
</table>

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Fig. 9 Nyquist plots (Z_re vs Z_im) for different photoelectrodes: Cu-1.0/Cu(OH)₂, Cu-1.0/Cu₂O, Cu-1.0/Cu₂O/Cu(OH)₂, and Cu-1.0/Cu₂O/CuO in the dark and under illumination.

Fig. 10 Mott-Schottky plot at a fixed frequency on Cu-1.0/Cu₂O/CuO composite electrode.
well as the tendency of the thus generated electrons and holes to recombine are both high. On the other hand, in the Cu2O/CuO composite, due to an appropriate band energy structure (Scheme 2), the photogenerated electrons from Cu2O are easily transferred to the conduction band of CuO where the recombination of the electrons and holes are considerably hindered because in CuO such a transition involves a phonon. Furthermore, CuO, having a narrower band gap than Cu2O, expands the solar absorption spectrum of the Cu2O/CuO composite, and thus further enhances its PEC performance.

4. Conclusions
In this study, a facile electrochemical strategy was proposed and successfully employed to synthesize highly stable and efficient copper oxide composite photocathode materials for PEC water splitting. The synthesis consisted of two steps. In the first step, a Cu film was electrodeposited on an ITO surface from a Cu(NO3)2 solution. By tuning the applied electrodeposition potentials, a desirable orientation of the formed Cu film could be achieved, which is pivotal for a high PEC performance of the synthesized composite materials. In the second step, the Cu film was anodized under a suitable current density, followed by calcination, to form the Cu2O/CuO composite material. The PEC water splitting activity of the composite materials was found to be strongly dependent on the chemical composition, preferred orientation, and crystalline degree of the materials. The Cu2O/CuO composite photocathode with Cu2O in (220) orientation showed the best PEC performance among all materials synthesized. The CuO nanostructure on top of Cu2O served not only as a protector minimizing Cu2O photo-corrosion but also as a recombination inhibitor for photogenerated electrons and holes from Cu2O to significantly promote the overall PEC activity of the composite materials. Therefore, the Cu2O/CuO composite material is believed to satisfy the necessary criteria as a promising photocathode material for PEC water splitting applications for artificial hydrogen generation.

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Notes and references