Insight into the origin of the limited activity and stability of p-Cu₂O films in photoelectrochemical proton reduction

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1. Introduction

One of the techniques that is emerging as a promising method for storage of renewable energy, is photocatalytic or photoelectrochemical splitting of water, yielding hydrogen (and oxygen) gas. Unfortunately, the efficiency of many cell configurations in solar-to-hydrogen conversion is low, because either the band gap of the applied semiconductors is too large and only photons of the UV region of the solar spectrum can be efficiently captured (i.e. TiO₂, ZnO and SrTiO₃), or the conduction band minimum is positioned unfavourably, so that water (proton) reduction is not thermodynamically feasible (for example the case for Fe₂O₃ and WO₃) [1,2]. In order to achieve overall water splitting using semiconductors with a small band gap, a two-photon system based on a Z-scheme can be employed, which requires two semiconductors (a H₂- and an O₂-evolving photocatalyst) that are electrically connected via an electron mediator [1,3,4]. Alternatively, both semiconductors can be connected through an Ohmic contact, constituting a so-called p-n type photoelectrochemical diode [5,6]. Recently, Zoontjes introduced an innovative design of a water splitting device, containing a Pt divider separating hydrogen and oxygen, which is simultaneously used as Ohmic contact between the photocathode and anode [7].

To date, many n-type oxide semiconductors have been reported to be promising photo-anodes stimulating water oxidation (i.e. WO₃ [8] and BiVO₄ [9]), but the efficiency and photoelectrochemical stability of p-type oxide semiconductors suitable for H₂ formation is limited. Despite development of novel p-type (oxide) photocathode materials such as CuFeO₂ [10] and Cu₂ZnSnS₄ [11], p-Cu₂O is still one of the most promising p-type oxide materials for photocatalytic and photoelectrochemical water splitting. p-Cu₂O has many favourable properties: it is abundant, cheap and environmentally benign, and its band gap of 1.9-2.2 eV is suitable for solar energy conversion in the visible light region [12-14]. Furthermore, the conduction band minimum lies significantly negative of the equilibrium potential of water reduction [14]. Unfortunately, the stability of p-Cu₂O is low and requires improvement. Cu₂O has a limited photoelectrochemical stability in aqueous solutions, since the redox potentials for the reduction and oxidation of Cu₂O to Cu and CuO, respectively, are located within its bandgap [14]. In previous reports, different strategies...
were employed for the enhancement of the photoelectrochemical stability of Cu2O, including atomic layer deposition of a layer of ZnO:Al and TiO2 with or without an additional RuO2 layer \cite{14,15}, protection with a layer of carbon \cite{16}, improvement of the crystallinity and reduction of defects by annealing \cite{17}, and chemical etching of the surface by MV2+/ reduction \cite{18}. The first three techniques have the advantage that the photocurrent was simultaneously enhanced with the stability (see Table 1), but their disadvantage is that the photocurrent still decreases significantly within the first 20 minutes; only the protection with an additional RuO2 layer seems to be capable of improving the photoelectrochemical stability of Cu2O as photocathode, showing 94% of its initial activity after 8 h of illumination \cite{15}. In another study from Sowers et al., it is proposed that the crystal orientation and surface termination of Cu2O play a significant role in determining its photoelectrochemical stability, and they show that Cu2+-terminated (111) surfaces are more stable than the more commonly obtained O2–-terminated (100) surfaces \cite{19}. Comparing the different electrolytes and potentials used in the literature to the Pourbaix diagram of Cu \cite{20}, surprisingly many photoelectrochemical measurements reported in the literature were performed at conditions in which Cu2O thermodynamically corrodes in the absence of illumination. From the Pourbaix diagram it can be observed that shifting the applied potential from 0 V vs. RHE to 0.3 V vs. RHE and by using an electrolyte with neutral pH, Cu2O is already more stable, and the use of a protective coating is not principally necessary \cite{20}. Therefore, we used these conditions (pH 7 and 0.3 V vs. RHE) in the present study for the evaluation of the photocatalytic activity of different Cu2O films deposited on a platinized Si substrate, serving as a model substrate for the metallic divider proposed by Zoonjtjes et al. \cite{7}. Furthermore, we studied the effect of different hole and electron scavengers on both the photocatalytic activity and the photoelectrochemical stability of Cu2O films in the absence or presence of a RuO2 layer, in order to evaluate the limiting factors that result in the poor performance of Cu2O. Although it is known that electron acceptors, such as H2O2, improve the stability of Cu2O, we provide more detail in the chemistry and Faradaic efficiency of these Cu2O films by combining PEC measurements with ultra-sensitive real-time Gas Chromatography measurements (allowing H2 and O2 detection in the ppb range).

2. Experimental details

All chemicals used were purchased from commercial sources and used without further purification. Copper sulphate pentahydrate (CuSO4·5H2O, p.a. quality) and sodium sulphate (Na2SO4, p.a. quality) were purchased from Boom Chemie; lactic acid (extra pure), sodium hydroxide (NaOH, purity 98.5%), sulfuric acid ([H2SO4, 96% in water] and dipotassium phosphate trihydrate ([K2HPO4·3H2O, purity >99%]) were purchased from Acros Organics; chloroplatinic acid hexahydrate ([H2PtCl6·6H2O, powder and chunks]), potassium ruthenium tetraoxide (K2RuO4), potassium sulphate (K2SO4, purity ≥ 99%), hydrogen peroxide (H2O2, 30 wt% in H2O), sodium persulphate (Na2S2O8, purity ≥ 98%), sodium sulphite (Na2SO3, purity 98-100%) and methanol were purchased from Sigma-Aldrich. Double distilled water with a resistivity of 18.2 MΩ·cm was used in all experiments.

Cu2O layers were made by electrodeposition on a platinized Si wafer as the working electrode. The platinized Si wafer was obtained by deposition of a layer of 13 nm Ti, and subsequently 100 nm Pt by sputtering, using a commercially available <100> Si wafer and a home-build sputtering setup, by applying a 6.6 mbar argon atmosphere and a 200 W direct current. A similar platinized Si wafer was used as counter electrode during the deposition procedure, and Ag/AgCl in 3 M KCl (Metrohm Autolab) was used as reference electrode. The electrodes were connected to an Autolab PGSTAT 128N potentiostat. p-Cu2O was deposited at −0.4 V vs. Ag/AgCl from an aqueous electrolyte containing 0.02 M CuSO4 and 0.4 M lactic acid. Before deposition, the solution was adjusted to pH 11 using NaOH and heated in a water bath to a temperature of 60 °C.

RuO2 layers were deposited by photo-enhanced electrodeposition in a different three-electrode cell connected to a Versastat 4 potentiostat (Princeton). Here, the working electrode was the previously deposited Cu2O film, the counter electrode consisted of a Pt mesh connected to a Pt wire, and Ag/AgCl in 3 M KCl (BASI) was used as the reference electrode. The reactor consisted of a 25 ml optical glass cuvette (Hellma Analytics), which filtered most of the emitted UV light. In this cell, the RuO2 layer was deposited for 15 min at −33.7 μA/cm² from an aqueous solution containing 1.3 mM K2RuO4 under constant illumination with an AM 1.5G solar simulator (model 10500, ABET Technologies) \cite{15}.

Photoelectrochemical (PEC) measurements were performed in an electrolyte consisting of 0.1 M K2SO4 with or without an additional 0.1 M of an electron- or hole scavenger (H2O2, S2O82–, methanol, SO42–, PO43–). As a reference, the electrolyte described by Paracchino et al. \cite{10 M Na2SO4 with 0.1 M K2HPO4 at pH 4.9 was used \cite{14}. Linear Sweep Voltammetry (LSV) curves were measured as part of a cyclic voltammogram (CV), measured in the positive direction from −0.5 V vs. Ag/AgCl to 0.5 V vs. Ag/AgCl at 0.05 V/s, of which the second half of the first CV was taken as the LSV when the curve was measured in the negative direction from 0.5 V vs. Ag/AgCl to −0.5 V vs. Ag/AgCl. For prolonged PEC measurements, a 300 W Xe lamp with AM 1.5G filter (Newport Corporation) with an automatic shutter was used in combination with the same electrochemical cell and potentiostat. The potential was converted to the RHE reference electrode by the Nernst equation:

\[
E(\text{vs. RHE}) = E(\text{vs. Ag/AgCl}) + E_{\text{Ag/AgCl}}(\text{ref}) + 0.0591 \cdot \text{pH}(1)
\]

Next to the PEC measurements, the photoelectrochemical stability of the Cu2O films before and after PEC measurements was evaluated by XRD and SEM. For analysis of the crystal structure of Cu2O and the presence of Cu and/or CuO in the Cu2O layers, a Bruker D2 powder diffractometer (equipped with a Cu Kα source) was used. A Nova 600-nanolab HRSEM instrument (FEI Instruments) was used for imaging of the Cu2O surface.

Gas Chromatography (GC) measurements were performed in combination with the PEC measurements in order to investigate

<table>
<thead>
<tr>
<th>Stability enhanced by</th>
<th>Electrolyte used</th>
<th>Potential used (V vs. RHE)</th>
<th>Photocurrent obtained (mA/cm²)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>ALD of ZnO:Al and TiO2</td>
<td>1.0 M Na2SO4 and 0.1 M K2HPO4 (pH 4.9)</td>
<td>0</td>
<td>−7.6</td>
<td>[14]</td>
</tr>
<tr>
<td>ZnO:Al, TiO2 and RuO2</td>
<td>0.5 M Na2SO4 and 0.1 M K2HPO4 (pH 5.0)</td>
<td>0</td>
<td>−5</td>
<td>[15]</td>
</tr>
<tr>
<td>C layer protection</td>
<td>1.0 M Na2SO4 (pH 7)</td>
<td>0</td>
<td>−3.95</td>
<td>[16]</td>
</tr>
<tr>
<td>Annealing</td>
<td>0.5 M Na2SO4 (pH 7)</td>
<td>0.3</td>
<td>−0.143</td>
<td>[17]</td>
</tr>
<tr>
<td>Surface etching</td>
<td>0.5 M Na2SO4 and 20 mM MV2+ (pH 5)</td>
<td>0</td>
<td>−0.25</td>
<td>[18]</td>
</tr>
</tbody>
</table>

Table 1 Overview of stability enhancement strategies and obtained photocurrents of Cu2O.
the mechanistic aspects involved in the photoelectrochemical water splitting of the Cu2O-RuO2 films in the different electrolytes. To this end, a Compact GC (Interscience) equipped with a pulsed discharge detector (PDD) was used with a 7N helium purge of 10 mL/min. The combined GC and PEC measurements were performed in a home-build PEC cell with a quartz window and a gas inlet and outlet for the GC measurements. Before each measurement, the electrolyte was purged with He overnight to remove as much O2 and N2 from the solution as possible. The next morning, the O2 deficient electrolyte was inserted into the PEC cell and purged for 1 hour before starting the GC measurement.

3. Results and discussion

Fig. 1a shows the surface of an as-deposited Cu2O film with cubic crystals ranging in size from 100 nm to 1 μm. The XRD pattern shown in Fig. 1c (black curve) demonstrates that Cu2O crystals grow preferentially in the (111) direction with a minor fraction in the (220) direction, induced by the presence of lactic acid in the precursor solution. Also, a small Cu peak was observed, which was apparently deposited along with Cu2O. The Pt diffraction line is due to the Pt film present on Si, used as a substrate for the Cu2O film. After photoelectrochemical (PEC) measurements for 30 min in neutral solution (0.1 M K2SO4, pH 7), it was observed that the surface of the Cu2O crystals roughened (Fig. 1b). As the XRD patterns of the samples before and after PEC measurements are similar (Fig. 1c), it is expected that roughening only took place at the top surface and did not largely affect the crystal integrity of Cu2O. Most importantly, no additional peaks for metallic Cu were found for the XRD measurement of the p-Cu2O film after PEC measurement. As can be seen from Fig. 1d, the measured photocurrent was quite stable and decreased only by ~10% in the first few minutes, followed by stable performance in the remainder of the measurement (30 min total). Also, the dark current only slightly increased during the first few min of measurement, but then stayed constant. However, it should be noted that we observed a much smaller photocurrent density than values reported in the literature at 0.3 V [14]. This total current density of ~0.06 mA/cm² yields the equivalent of 0.11 C/cm² passed through the cell after 30 min. Assuming all charge is used to reduce Cu2O to metallic copper (2 electrons per Cu2O unit), a maximum of 136 nm of Cu2O is reduced (using the molar mass of Cu2O of 143 g/mol, and a density of 6 g/cm³). As this is only about 7% of the total thickness of the film (~2.5 μm according to the SEM cross section, see Fig. 3b), this could explain the observed degradation being limited to the top surface of the p-Cu2O film (Fig. 1b). Furthermore, we observed large cathodic and anodic spikes in current when the light was turned on and off, respectively; these spikes indicate significant accumulation and recombination of photoexcited states (charges), suggesting that the H2 evolution rate is low compared to the formation rate of electron-hole pairs by light absorption [21].

Even though the measurement conditions used seemed to provide a relatively higher photoelectrochemical stability, the photocurrent density of ~0.06 mA/cm² as measured under these conditions is far from ideal for its use as a photocathode. To confirm that the large transient in photocurrent upon switching the light on or off is due to limiting catalytic performance of the p-Cu2O films for reduction of water, we investigated whether reduction of H2O2 or S2O8 2− (electron scavengers) would enhance the photocurrent [22,23]. The result is shown in Fig. 2. Both the use of H2O2 (red curve) and S2O8 2− (green curve) resulted in a significant increase in the photocurrent, as well as an increase in the dark current (Fig. 2a). Especially noteworthy is the observed stability in photocurrent for the sample with H2O2 added; after 27 min of illumination, the current densities as measured under illumination and in the dark were even slightly higher as observed after 10 min of illumination, while slightly increasing their difference. Furthermore, the large and fast cathodic and anodic spikes as observed in Fig. 1d were not observed in a H2O2 containing solution, indicating electron transfer to H2O2 is quite efficient. The origin of the slow transient in current response (to less negative values) after illumination was switched off is not exactly understood, but might be related to passivation of the photochemically active surface states of the Cu2O cathode. The XRD pattern of this sample did not show significant differences before and after experiment, and only a minor change in sample surface structure was observed (red curve in Fig. 2b, and Fig. 2c, respectively). The enhancement in current density upon illumination using H2O2 as scavenger was ~0.94 mA/cm².

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Fig. 1. (a,b) Top-view SEM images of a Cu2O film (a) before and (b) after PEC measurement in 0.1 M K2SO4 (pH 7) for 30 min at an applied potential of 0.3 V vs. RHE; (c) XRD pattern of the Cu2O film before (black curve) and after (blue curve) photocurrent measurement: Diffraction peaks can be assigned to Pt (JCPDS # 88-2343), Cu2O (JCPDS # 05-0667) and Cu (JCPDS # 03-1018); (d) PEC measurement of the Cu2O film in 0.1 M K2SO4 at an applied potential of 0.3 V vs. RHE: the light was turned on and off during the PEC measurement (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
Fig. 2. (a) PEC measurements of p-Cu2O films in 0.1 M K2SO4 with and without scavengers: (blue curve) no scavenger, (red curve) 0.1 M H2O2 and (green curve) 0.1 M Na2S2O8; the (magenta curve) was measured in an aqueous solution containing 1.0 M Na2SO4 with 0.1 M K2HPO4 at pH 4.9; all measurements were performed at an applied potential of 0.3 V vs. RHE and the light was turned on and off during the measurements; (b) XRD patterns of the Cu2O films (black curve) before and after photocurrent measurements (same color index as in (a)); Diffraction peaks were assigned to Pt (JCPDS # 88-2343), Cu2O (JCPDS # 05-0667) and Cu (JCPDS # 03-1018); (c-e) top-view SEM images of Cu2O films after PEC measurement in 0.1 M K2SO4 with (c) 0.1 M H2O2 or (d) 0.1 M Na2S2O8 at pH 7, and in (e) 1.0 M Na2SO4 with 0.1 M K2HPO4 at pH 4.9 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Fig. 3. (a) Top-view and (b) cross-section SEM images of a Cu2O film with a RuO2 top layer; (c) PEC measurement of Cu2O-RuO2 films in 0.1 M K2SO4 with and without scavengers: (blue curve) no scavenger, (red curve) with 0.1 M H2O2 and (green curve) with 0.1 M Na2S2O8; all measurements were performed at an applied potential of 0.3 V vs. RHE and the light was turned on and off during the measurements in order to obtain a better insight into the difference between the photocurrent and the dark current; (d-f) top-view SEM images of Cu2O-RuO2 films after PEC measurement in 0.1 M K2SO4 (d) without scavenger, (e) with 0.1 M H2O2 and (f) with 0.1 M Na2S2O8 (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
Using $S_2O_8^{2-}$ as electron scavenger, the current increase between dark and illuminated operation was high and amounted to $-1.34$ mA/cm$^2$. However, as can be seen from Fig. 2a, the obtained current was not stable during the duration of the measurement as both the current density under illumination and in the dark increased significantly over time. This increase can be related to a change in morphology and an increase in surface area of the electrode as observed in Fig. 2d, although a minor contribution from Pt cross-over from anode to cathode cannot be excluded. As the XRD pattern (green curve in Fig. 2b) does not show a phase change, this might indicate that Cu$_2$O photoelectrodes slowly dissolve when exposed to electrolytes containing $S_2O_8^{2-}$. In addition, it should be noted that $S_2O_8^{2-}$-reduction (reactions (3) and (4)) induces current doubling when used as an electron scavenger:

$$S_2O_8^{2-} + e^- \rightarrow SO_4^{2-} + \frac{1}{2}O_2 \quad (3)$$

$$SO_4^{2-} + H_2O \rightarrow SO_2^{3-} + OH^- + H_2O \quad (4)$$

where • denotes a radical. Reaction (1) requires photon absorption (one photon per electron), while current doubling occurs due to subsequent reaction of the formed OH$^-$ radicals to OH$^-$ (accepting a second electron (not requiring an absorbed photon)) [24]. Therefore, the increase in photocurrent might not necessarily scale with an increase in Cu$_2$O induced photon efficiency.

It should be noted that the possibility of photocurrent doubling (due to the formation of OH$^-$ radicals by $H_2O + e^- \rightarrow OH^- + OH^-$) is also suggested for the use of $H_2O_2$ [25–28], and that especially in the case of GaAs, the cathodic reduction of $H_2O_2$ was associated with chemical etching of the GaAs surface [26,27]. In this respect, we would like to stress that in the case of p-Cu$_2$O electrodes, we observed the opposite effect, namely a higher photoelectrochemical stability of the Cu$_2$O films upon addition of $H_2O_2$. Since the extent of photocurrent doubling is strongly dependent on the semiconductor used, as well as on its surface orientation and the applied light intensity, the contribution of current-doubling to the enhancement in photocurrent induced by $H_2O_2$ cannot be easily quantified and requires further investigation.

Finally, the electrolyte that was previously used by Paracchino et al. (1.0 M Na$_2$SO$_4$ with 0.1 M KH$_2$PO$_4$ at pH 4.9) was used (magenta curve in Fig. 2a) [14]. As expected from their publication and the Pourbaix diagram of copper, the obtained photocurrent in this solution quickly diminished as the Cu$_2$O layer reduced to Cu. The observed difference between photocurrent and dark current was minimal after 10 min of illumination. Instability of this Cu$_2$O film was also clearly visible when analysing the sample surface, which turned into nanoparticles with a diameter of ~40 nm while maintaining the overall cubic structure typical for Cu$_2$O films (Fig. 2e). Furthermore, an additional and significant Cu peak was found in the XRD pattern of this film (Fig. 2b, magenta curve), in agreement with the black colour of this sample after measurement.

Additionally, also the use of the well-known hole scavengers methanol and $SO_3^{2-}$ was investigated, as well as the use of $PO_4^{3-}$ at pH 7, but these electrolytes did not show any difference in behaviour compared to the electrolyte without added scavenger (results not shown).

Although the previous results indicated a lower rate of photodissolution of Cu$_2$O under the conditions used here, the additional protective effect of RuO$_2$ deposited directly on top of the Cu$_2$O film was also evaluated under these conditions. The RuO$_2$ layer consists of small amorphous nanoparticles merged together into a continuous film following the overall morphology of the underlying Cu$_2$O film, as was observed by SEM (Fig. 3a and b) and the lack of additional XRD lines (shown below in Fig. 6g (black curve)). The PEC chronogram for the Cu$_2$O-RuO$_2$ sample measured in an electrolyte without scavenger (blue curve in Fig. 3c) shows a very low transient current response after the light source was turned on or off. When $H_2O_2$ or $SO_3^{2-}$ are added to the solution, an increase in dark current and photocurrent is apparent, as was also the case for Cu$_2$O samples without RuO$_2$ (Fig. 2a). Comparing the photodissolution values of the samples with and without RuO$_2$, it can be observed that the photocurrent decreased upon addition of the RuO$_2$ layer (-0.43 mA/cm$^2$ vs. -0.94 mA/cm$^2$ and -0.30 mA/cm$^2$ vs. -1.34 mA/cm$^2$ for $H_2O_2$ and $SO_3^{2-}$ respectively), but the stability increased significantly; the performance is particularly stable when $H_2O_2$ is present in the electrolyte (Fig. 3c). As can be seen from Fig. 3e, the PEC measurement with added $H_2O_2$ did not influence the morphology of the Cu$_2$O-RuO$_2$ sample at all, while the morphology of the sample containing RuO$_2$ also appeared stabilized in the absence of a scavenger (Fig. 3d). On the other hand, the morphology of the sample in the presence of $S_2O_8^{2-}$ changed dramatically (Fig. 3f), which indicates that $S_2O_8^{2-}$ is so corrosive, that a RuO$_2$ protection layer becomes ineffective.

A linear sweep voltammetry (LSV) in the dark and under illumination provides information about the onset potential of a photocathode in a specific electrolyte, which is a measure of the required overpotential for $H_2$ evolution and therefore a measure for the suitability of the photocathode for water splitting. When connecting the photocathode to a photoanode in a photoelectrochemical diode, a more positive onset potential is highly desirable [29]. Fig. 4 shows a selection of LSV curves measured in light and dark conditions on different samples (Cu$_2$O and Cu$_2$O-RuO$_2$) with or without the addition of $H_2O_2$ or $SO_3^{2-}$ to the electrolyte. From this figure, it can be observed that the onset potential for a Cu$_2$O film without the use of an electron scavenger (0.4 V vs. RHE) is very close to the potential used for chronoamperometric measurements (0.3 V vs. RHE), which explains the low current densities observed for this sample. Both the addition of $H_2O_2$ and $SO_3^{2-}$ provided an onset potential of 0.8 V vs. RHE, explaining the much higher current densities in the presence of these compounds. When a Cu$_2$O-RuO$_2$ film is measured without

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**Fig. 4** LSV measurements of: (dark blue curves) Cu$_2$O film in 0.1 M K$_2$SO$_4$ (red curves), Cu$_2$O film in 0.1 M K$_2$SO$_4$ and 0.1 M H$_2$O$_2$ (green curves), Cu$_2$O film in 0.1 M K$_2$SO$_4$ and 0.1 M Na$_2$S$_2$O$_8$ (light blue curves), Cu$_2$O-RuO$_2$ film in 0.1 M K$_2$SO$_4$ and (magenta curves) Cu$_2$O-RuO$_2$ film in 0.1 M K$_2$SO$_4$ and 0.1 M H$_2$O$_2$. For all samples, the solid curve was measured under AM 1.5G illumination, and the dotted curve was measured in the dark (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
scavenger, the onset potential lies even more positive than 1.1 V vs. RHE, while the difference between the dark current and the current measured under illumination is small. When measuring a Cu2O-RuO2 sample with H2O2 added, the onset potential becomes slightly more negative (1.0 V vs. RHE), while the difference between the dark current and the current measured under illumination is more pronounced at potentials more negative than 0.6 V vs. RHE. At more positive potentials, the difference between the current measured under illumination and in the dark stays rather low for these measurement conditions.

The photoelectrochemical stability of a Cu2O-RuO2 film was further investigated during a long-term PEC measurement in which H2O2 was added to the electrolyte (Fig. 5). Fig. 5a shows that the photocurrent decreases from −1.9 mA/cm² to −1.0 mA/cm² during the first 7 hours of the measurement, but increased again after addition of fresh H2O2. Therefore, this decrease in photocurrent can be ascribed to the consumption of H2O2. Fig. 5b shows that this Cu2O-RuO2 sample was photoelectrochemically stable even after more than 11 hours of illumination, which underlines the importance of fast electron extraction from the photocathode for improved stability.

In order to analyse the cathodically induced chemical transformations, we performed PEC measurements in a cell that was connected to a gas chromatograph (GC) (Fig. 6; see Fig. 6g for a schematic representation of the cell). In Fig. 6a,c,e, the results from the combined PEC and GC measurements are shown, in which the amounts of H2 and O2 evolved during the measurement are directly compared to the measured current density. From the measurement without scavenger (Fig. 6a), it can be seen that both H2 and O2 evolved from the PEC cell upon illumination of the Cu2O-RuO2 film while applying a bias of 0.3 V vs. RHE, but they did not evolve in a 2:1 ratio as would be expected from stoichiometric water splitting; much more O2 than H2 evolved. We propose the following reactions taking place on a Cu2O-RuO2 cathode and a Pt anode in 0.1 M K2SO4 (pH 7):

\[
\text{Oxidation: } H_2O_2 + 2H^+ \rightarrow 2H_2O + 1/2O_2 \quad E^\circ = -1.299 V_{\text{RHE}}
\]

(on PtCE) \[
\text{Reduction: } 2H^+ + 2e^- \rightarrow H_2, \quad E^\circ = 0 V_{\text{RHE}} \quad E = -0.413 V_{\text{RHE}}
\]

(6)

The transient in H2 evolution (peak in Fig. 6a) can be explained by the rapidly rising oxygen concentration in the cell. Even though a continuous purge is applied, we suspect that the reaction of hydrogen with oxygen to form water becomes significant (the ‘back reaction’, presumably occurring over the Pt anode). At the same time, the high concentration of oxygen formed can only be explained by a sacrificial reduction reaction, which suggests that despite the RuO2 film a significant fraction of Cu2O is in contact with the 0.1 M K2SO4 electrolyte, reacting according to reaction (5). The formation of Cu is indeed observed by XRD (blue curve in Fig. 6g). It should also be noted that the O2 evolution still continues after the solar simulator was turned off. This can likely be explained by the formed Cu particles, decreasing the cathode resistance, and allowing electrochemical O2 formation (anode) and reduction of Cu2O (cathode) to continue at the applied potential (0.3 V vs. RHE). As soon as the potential was released from the sample, the O2 formation rate dropped to zero within a few minutes, following the transient behaviour of the reactor.

For the sample for which H2O2 was used as electron scavenger, H2 and O2 were formed upon photoelectrochemical reaction (Fig. 6c). During the measurement, it was observed that gas bubbles accumulated on the sample surface before being released, which explains the sharp spikes in the GC signals and the continuous change in the measured current density. Both H2 and O2 evolved at a larger rate than for the sample without scavenger, but again did not evolve in a 2:1 ratio; again much more O2 than H2 evolved. Contrary to the sample without scavenger, Cu peaks were absent in the XRD spectra for this sample after reaction (red curve in Fig. 6g), and also the structure of the sample surface stayed more or less intact (Fig. 6d). This means that in this case the photoreduction of Cu2O to Cu is not the competing reaction with H2 formation, but the reduction of H2O2 to H2O (reaction (11)). This confirms that H2O2 is indeed used as an electron scavenger during photoelectrochemical water splitting using a Cu2O–RuO2 film. Since no Cu is formed in this case, no O2 was formed after the light source was turned off while the potential was still applied. Furthermore, Pt from the substrate and/or the counter electrode can also act as a catalyst for hydrogen peroxide decomposition (reaction (12)), which contributes to the nonstoichiometric H2 and O2 formation. Especially the much more than 5 times increase in observed O2 evolution in the case of added H2O2 as compared to the measurement without added electron scavenger (compare Fig. 6a,c with Fig. 3c) and the observed O2 formation before (and after) illumination, show the significance of this catalytic disproportionation reaction. In summary, with the use of H2O2 as an electron scavenger, the following reactions take place:

![Fig. 5.](image-url)
Fig. 6. (a, c, e) Combined PEC (at 0.3 V vs. RHE) and GC measurements of Cu2O-RuO2 films in (a) 0.1 M K2SO4 without scavenger, (c) 0.1 M K2SO4 with 0.1 M H2O2 and (e) 1 M Na2SO4 and 0.1 M K2HPO4 adjusted to pH 4.9. (b, d, f) Top-view SEM images of the Cu2O-RuO2 films after combined PEC and GC measurements in (b) 0.1 M K2SO4, (d) 0.1 M K2SO4 and 0.1 M H2O2, and (f) 1 M Na2SO4 and 0.1 M K2HPO4 at pH 4.9. (g) Schematic representation of the PEC cell used for the combined PEC and GC measurements showing the ideal case of stoichiometric water splitting; for simplicity, the Ag/AgCl reference electrode used is not shown. (h) XRD measurements of the Cu2O-RuO2 films (black curve) before and (blue, red, magenta curves) after combined PEC and GC measurements in (blue curve) 0.1 M K2SO4, (red curve) 0.1 M K2SO4 and 0.1 M H2O2, and (magenta curve) 1 M Na2SO4 and 0.1 M K2HPO4 at pH 4.9: Diffraction peaks were assigned to Pt (JCPDS # 88-2343), Cu2O (JCPDS # 05-0667) and Cu (JCPDS # 03-1018) (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).
Oxidation: \( H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \) and \( E^* = -1.229 \text{ VRHE} \)
\( E = -0.816 \text{ VRHE} \) (8)

(\text{on Pt CE}) \( H_2O_2 + 2OH^- + 2h^+ \rightarrow O_2 + 2H_2O \), \( E^* = 0.146 \text{ VRHE} \)
\( E = -0.297 \text{ VRHE} \) (9)

Reduction: \( 2H^+ + 2e^- \rightarrow H_2 \) and \( E^* = 0 \text{ VRHE} \)
\( E = -0.413 \text{ VRHE} \) (10)

(\text{on Cu}_2O-RuO_2) \( H_2O_2 + 2H^+ + 2e^- \rightarrow 2H_2O \), \( E^* = 1.776 \text{ VRHE} \)
\( E = 1.334 \text{ VRHE} \) (11)

Catalysis: (on Pt) \( 2H_2O_2 \rightarrow O_2 + 2H_2O. \) (12)

For the sample that was measured in an electrolyte at pH 4.9, as was previously used by Paracchino et al. [14], \( H_2 \) formation was not significant and predominantly \( O_2 \) was formed (Fig. 6e). Furthermore, we observed that this sample lost its electrical contact after approximately 1 hour of PEC measurement. It was attempted to restart the PEC measurement, but as can be observed from the large switching of the current density around 2:15 hours, the contact with the sample was not regained. When the sample was taken out of the PEC cell, it was observed that the film was detached from the Si/Pt substrate, and SEM confirmed that the sample was reduced during the measurement (Fig. 6f), in agreement with the presence of a significant Cu peak in the XRD spectrum after the measurement (magenta curve in Fig. 6g). During the period that the potential was applied to the sample without having proper contact, it was observed that \( O_2 \) formed, and the \( O_2 \) formation went back to 0 after the potential was turned off while the light was still turned on. This dependence of the \( O_2 \) formation on the availability of an applied potential to the sample and not on the availability of light can be ascribed to the formation of Cu on this sample. In summary, with the use of Na_2SO_4 and K_2HPO_4 as the electrolyte at pH 4.9, the following reactions take place on a CuO-RuO_2 film:

Oxidation: \( H_2O + 2h^+ \rightarrow 2H^+ + \frac{1}{2}O_2 \) and \( E^* = -1.229 \text{ VRHE} \)
\( E = -0.816 \text{ VRHE} \) (13)

(\text{on Pt CE}) \( H_2O_2 + 2OH^- + 2h^+ \rightarrow 2Cu + 2OH^- \),
\( E = -0.360 \text{ VRHE} \)
\( E = 0.053 \text{ VRHE} \) (14)

In summary, Fig. 7 shows the location of the valence and conduction band of Cu_2O including the position of all redox reactions (reactions (5)-(14)) as discussed above. The reactions indicated in red and blue are the reactions that take place in the presence and absence of \( H_2O_2 \) in the electrolyte, respectively, as observed by the GC measurements shown in Fig. 6. As can be seen in Fig. 7, for both cases (with or without \( H_2O_2 \)) these colored redox reaction pairs correspond to the reduction reaction with the most negative redox potential possible in combination with the oxidation reaction with the most positive redox potential possible. Furthermore, we can observe that the redox reactions involving \( H_2O_2 \) (in red) are thermodynamically able to take place spontaneously without the presence of illuminated Cu_2O, as was also observed in Fig. 6c, although the presence of illuminated Cu_2O did increase the efficiency of these reactions. The energetically more favorable redox reactions without \( H_2O_2 \) added to the electrolyte (in blue) do need the presence of illuminated Cu_2O in order to take place, as was also observed in Fig. 6c and Fig. 6e.

The activity determination and evaluation of structural changes confirm that the performance and stability of (RuO_2 protected) Cu_2O can be significantly improved if efficient electron transfer is induced, which could be achieved by an efficient proton reduction catalyst. As our data show that RuO_2 is not sufficiently effective for this purpose [17,30], we also performed preliminary experiments with additional Pt nanoparticles. These preliminary experiments in our laboratory have shown that deposition of Pt particles on top of Cu_2O and CuO-RuO_2 films, without modification of the composition and structure of Cu_2O, is not trivial, and photodeposition of Pt particles resulted in an insignificant current density increase as compared to that obtained in the presence of \( H_2O_2 \). Non-destructive Pt deposition by physical methods such as sputtering or e-beam evaporation is highly desired for obtaining more efficient and stable Cu_2O photocathodes. Indeed, Grätzel and co-workers already solved this issue by applying their champion bilayer coating of Al-doped ZnO and TiO_2 via atomic layer deposition (ALD), after which they were able to successfully deposit Pt by either photodeposition or E-beam evaporation [14,15]. On the other hand, we would like to emphasize here, that in this work we tried to work around the necessity of these ALD coatings, which would make the final photocathode system more easily scalable. Provided that Pt nanoparticles or another hydrogen evolution catalyst can be deposited with a non-destructive and scalable deposition technique on top of the CuO-RuO_2 films, our experiments show that it should indeed be possible to obtain photoelectrochemically more stable p-Cu_2O photocathodes without the need to grow passivation layers via ALD.

Another method for improvement of the efficiency of p-Cu_2O as a photocathode in photoelectrochemical water splitting would be to use nanostructures like nanowires, nanowire networks or nanowires [31]. Especially for Cu_2O with a diffusion length of minority charge carriers (electrons in the case of p-Cu_2O) of only 20–100 nm, and an absorption depth near the bandgap of approximately 10 µm [16,32–34], the use of one-dimensional...
nanostructures is likely to be highly beneficial to increase photocurrent efficiencies [35].

4. Conclusions

It was found that the photoelectrochemical stability of p-Cu2O films used for photoelectrochemical water splitting can be significantly enhanced by the use of milder conditions (pH 7 and 0.3 V vs. RHE) than typically applied in the literature. Although a photoelectrodeposited RuO2 layer further enhanced the stability, the measured photocurrent slightly decreased. Significant performance was obtained when H2O2 was added as an electron scavenger to the electrolyte: the measured photocurrent (for H2O2 reduction) was increased and also the photoelectrochemical stability was that high, that the Cu2O-RuO2 film could be illuminated for more than 11 hours without noticeable photo-reduction to Cu. By combining gas chromatography with the performed photoelectrochemical measurements, it was confirmed that H2O2 served as an electron scavenger during photoelectrochemical water splitting using Cu2O-RuO2 films: therefore, the addition of a suitable H2 evolution catalyst is highly recommended for obtaining more efficient Cu2O photocathodes. Unfortunately, Pt nanoparticles prepared by photodeposition appeared incapable of providing high hydrogen production rates and stability.

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