Insight into the origin of the limited activity and stability of p-Cu$_2$O films in photoelectrochemical proton reduction

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The origin of instability of p-Cu$_2$O films deposited on a platinized Si substrate when used as photocathode in photoelectrochemical water splitting, was studied in the absence or presence of a protective layer of RuO$_2$. When applied at +0.3 V vs. RHE and at pH 7, p-Cu$_2$O films were found to show a slightly more stable performance as compared to photoelectrochemical measurements reported in the literature at 0 V vs. RHE and under acidic conditions. In addition, the stability and the photocurrent induced by the Cu$_2$O films were significantly improved when H$_2$O$_2$ was added to the electrolyte, which is explained by efficient scavenging of electrons, yielding oxygen and water as confirmed by gas chromatography (GC). Also, other electron acceptors improved the photocatalytic performance of the p-Cu$_2$O films, demonstrating that the transfer of photo-excited electrons to protons adsorbed on the surface is the rate determining step in p-Cu$_2$O based photo-electrochemical water splitting. We confirmed that deposition of RuO$_2$ improves the stability of the films, but to the expense of a decrease in photocurrent density. The results provided in this study rationalize the attachment of an effective H$_2$ evolution catalyst as a means to significantly improve the stability of p-Cu$_2$O electrodes.

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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. TiO$_2$, ZnO and SrTiO$_3$), or the conduction band minimum is positioned unfavourably, so that water (proton) reduction is not thermodynamically feasible (for example the case for Fe$_2$O$_3$ and WO$_3$) [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 H$_2$- and an O$_2$-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. WO$_3$ [8] and BiVO$_4$ [9]), but the efficiency and photoelectrochemical stability of p-type oxide semiconductors suitable for H$_2$ formation is limited. Despite development of novel p-type (oxide) photocathode materials such as CuFeO$_2$ [10] and Cu$_2$ZnSnS$_4$ [11], p-Cu$_2$O is still one of the most promising p-type oxide materials for photocatalytic and photoelectrochemical water splitting. p-Cu$_2$O 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-Cu$_2$O is low and requires improvement. Cu$_2$O has a limited photoelectrochemical stability in aqueous solutions, since the redox potentials for the reduction and oxidation of Cu$_2$O to Cu and CuO, respectively, are located within its bandgap [14]. In previous reports, different strategies

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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 [14,15], protection with a layer of carbon [16], improvement of the crystallinity and reduction of defects by annealing [17], and chemical etching of the surface by MV2+ reduction [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 [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 [19].

Comparing the different electrolytes and potentials used in the literature to the Pourbaix diagram of Cu [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 [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 planarized Si substrate, serving as a model substrate for the metallic divider proposed by Zoonjtjes et al. [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 pertruhenate (KRuO4), 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 planarized Si wafer as the working electrode. The planarized 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 planarized 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 KRuO4 under constant illumination with an AM 1.5G solar simulator (model 10500, ABET Technologies) [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, SO2, methanol, SO22−, PO43−). As a reference, the electrolyte described by Paracchino et al. [10 M Na2SO4 with 0.1 M K2HPO4 at pH 4.9] was used [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:

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

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-nanobal 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

| Stability enhanced by | Electolyte used | Potential used (V vs. RHE) | Photocurrent obtained (mA/cm²) | Ref. |
|----------------------|-----------------|----------------------------|--------------------------------|-----|
| ALD of ZnO:Al and TiO2 | 1.0 M Na2SO4 and 0.1 M K2HPO4 (pH 4.9) | 0 | −7.6 | [14] |
| ZnO:Al, TiO2, and RuO2 | 0.5 M Na2SO4 and 0.1 M K2HPO4 (pH 5.0) | 0 | −5 | [15] |
| C layer protection | 1.0 M Na2SO4 (pH 7) | 0 | −3.95 | [16] |
| Annealing | 0.5 M Na2SO4 (pH 7) | 0.3 | −0.143 | [17] |
| Surface etching | 0.5 M Na2SO4 and 20 mM MV²⁺ (pH 5) | 0 | −0.25 | [18] |
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 extra 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 S2O8²⁻ (electron scavengers) would enhance the photocurrent [22,23]. The result is shown in Fig. 2. Both the use of H2O2 (red curve) and S2O8²⁻ (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 photoelectrochemically 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.

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 $p$-Cu$_2$O films in 0.1 M K$_2$SO$_4$ with and without scavengers: (blue curve) no scavenger, (red curve) 0.1 M H$_2$O$_2$ and (green curve) 0.1 M Na$_2$S$_2$O$_8$; the (magenta curve) was measured in an aqueous solution containing 1.0 M Na$_2$SO$_4$ with 0.1 M K$_2$HPO$_4$ 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 Cu$_2$O films (black curve) before and after photocurrent measurements (same color index as in (a)); Diffraction peaks were assigned to Pt (JCPDS # 88-2343), Cu$_2$O (JCPDS # 05-0667) and Cu (JCPDS # 03-1018); (c-e) top-view SEM images of Cu$_2$O films after PEC measurement in 0.1 M K$_2$SO$_4$ with (c) 0.1 M H$_2$O$_2$ or (d) 0.1 M Na$_2$S$_2$O$_8$ at pH 7, and in (e) 1.0 M Na$_2$SO$_4$ with 0.1 M K$_2$HPO$_4$ 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.).
Using $\text{SO}_3^{2-}$ as electron scavenger, the current increase between dark and illuminated operation was high and amounted to $-1.34 \text{ mA/cm}^2$. 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 photo-electrodes slowly dissolve when exposed to electrolytes containing $\text{SO}_3^{2-}$. In addition, it should be noted that $\text{SO}_3^{2-}$ reduction (reactions (3) and (4)) induces current doubling when used as an electron scavenger:

$$\text{SO}_3^{2-} + e^- \rightarrow \text{SO}_4^{2-} + \frac{1}{2}\text{O}_2 \tag{3}$$

$$\text{SO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{SO}_4^{2-} + \text{OH}^- + \text{H}_2\text{O} \tag{4}$$

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 $\text{H}_2\text{O}_2$ + e$^-$ → OH$^-$ + OH) is also suggested for the use of $\text{H}_2\text{O}_2$ [25–28] and that especially in the case of GaAs, the cathodic reduction of $\text{H}_2\text{O}_2$ 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 observed effect, namely a higher photoelectrochemical stability of the Cu$_2$O films upon addition of $\text{H}_2\text{O}_2$. 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 $\text{H}_2\text{O}_2$ cannot be easily quantified and requires further investigation.

Finally, the electrolyte that was previously used by Paracchino et al. (1.0 M Na$_2\text{SO}_4$ with 0.1 M K$_2\text{HPO}_4$ 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 $\text{SO}_3^{2-}$ 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 photoreduction 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. 6 g (black curve)). The PEC chronocoulompermeter 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 $\text{H}_2\text{O}_2$ or $\text{SO}_3^{2-}$ 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 photocurrent 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$_2$O$_2$ and $\text{SO}_3^{2-}$, respectively), but the stability increased significantly; the performance is particularly stable when H$_2$O$_2$ is present in the electrolyte (Fig. 3c). As can be seen from Fig. 3e, the PEC measurement with added H$_2$O$_2$ 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 $\text{SO}_3^{2-}$ changed dramatically (Fig. 3f), which indicates that $\text{SO}_3^{2-}$ is so corrosive, that a RuO$_2$ protection layer becomes ineffective.

A linear sweep voltammetric (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 $\text{H}_2\text{O}_2$ or $\text{SO}_3^{2-}$ 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 $\text{H}_2\text{O}_2$ and $\text{SO}_3^{2-}$ 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
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):

\[
\text{Oxidation: } \quad \begin{align*}
H_2O + 2h^+ &\rightarrow 2H^+ + \frac{1}{2}O_2 \quad \text{E} = -1.299V_{\text{RHE}} \\
E &\downarrow = -0.816V_{\text{RHE}}
\end{align*}
\]

(on PtCE)

\[
\text{Reduction: } \quad 2H^+ + 2e^- \rightarrow H_2 \quad \text{and} \quad E^\prime = 0V_{\text{RHE}} \quad \text{E} = -0.413V_{\text{RHE}}
\]

(on Cu2O-RuO2)

\[
\text{Cu}_2O + H_2O + 2e^- \rightarrow 2Cu + 2OH^- \quad E^\prime = -0.360V_{\text{RHE}}
\]

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 CuO (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. (a) Long-term PEC measurement of a Cu2O-RuO2 film in 0.1 M K2SO4 and 0.1 M H2O2 at an applied potential of 0.3 V vs. RHE and with chopped light. —0.1 mL H2O2 was added after 7 hours to bring its concentration back to −0.1 M; (b) top-view SEM image of the Cu2O-RuO2 film after long-term PEC measurement in 0.1 M K2SO4 and 0.1 M H2O2.

Image 39x108 to 279x429
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 \( E^\circ = -1.229 \text{V}_{\text{RHE}} \) \( E = -0.816 \text{V}_{\text{RHE}} \) (8)

(on Pt CE) \( \text{H}_2\text{O}_2 + 20\text{H}^+ + 2\text{h}^+ \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \) \( E^\circ = 0.146 \text{V}_{\text{RHE}} \) \( E = -0.297 \text{V}_{\text{RHE}} \) (9)

Reduction: \( 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2 \) and \( E^\circ = 0 \text{V}_{\text{RHE}} \) \( E = -0.413 \text{V}_{\text{RHE}} \) (10)

(on Cu$_2$O-RuO$_2$) \( \text{H}_2\text{O}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2\text{O} \) \( E^\circ = 1.776 \text{V}_{\text{RHE}} \) \( E = 1.334 \text{V}_{\text{RHE}} \) (11)

Catalysis: (on Pt) \( 2\text{H}_2\text{O}_2 \rightarrow \text{O}_2 + 2\text{H}_2\text{O} \) (12)

For the sample that was measured in an electrolyte at pH 4.9, as was previously used by Paracchino et al. [14], \( \text{H}_2 \) formation was not significant and predominantly \( \text{O}_2 \) 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 \( \text{O}_2 \) formed, and the \( \text{O}_2 \) formation went back to 0 after the potentiostat was turned off while the light was still turned on. This dependence of the \( \text{O}_2 \) 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$_2$SO$_4$ and K$_2$HPO$_4$ as the electrolyte at pH 4.9, the following reactions take place on a Cu$_2$O-RuO$_2$ film:

Oxidation \( \text{H}_2\text{O} + 2\text{h}^+ \rightarrow 2\text{H}^+ + \frac{1}{2} \text{O}_2 \) \( E^\circ = -1.229 \text{V}_{\text{RHE}} \) \( E = -0.816 \text{V}_{\text{RHE}} \) (13)

(on pt CE) \( \text{Cu}_2\text{O} + 2\text{H}^+ + 2\text{e}^- \rightarrow 2\text{Cu} + 2\text{OH}^- \) \( E^\circ = -0.360 \text{V}_{\text{RHE}} \) \( E = -0.053 \text{V}_{\text{RHE}} \) (14)

In summary, Fig. 7 shows the location of the valence and conduction band of Cu$_2$O including the position of all redox reactions (reactions (5)-(14)) as described above. The reactions indicated in red and blue are the reactions that take place in the presence and absence of H$_2$O$_2$ 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$_2$O$_2$) 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$_2$O$_2$ (in red) are thermodynamically able to take place spontaneously without the presence of illuminated Cu$_2$O, as was also observed in Fig. 6c, although the presence of illuminated Cu$_2$O did increase the efficiency of these reactions. The energetically more favorable redox reactions without H$_2$O$_2$ added to the electrolyte (in blue) do need the presence of illuminated Cu$_2$O 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$_2$O 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$_2$O and Cu$_2$O-RuO$_2$ films, without modification of the composition and structure of Cu$_2$O 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$_2$O$_2$. Non-destructive Pt deposition by physical methods such as sputtering or e-beam evaporation is highly desired for obtaining more efficient and stable Cu$_2$O photocathodes. Indeed, Grätzel and co-workers already solved this issue by applying their champion bi-layer 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 photoelectrocatalytic 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 Cu$_2$O-RuO$_2$ films, our experiments show that it should indeed be possible to obtain photoelectrochemically more stable p-Cu$_2$O photocathodes without the need to grow passivation layers via ALD.

Another method for improvement of the efficiency of p-Cu$_2$O as a photocathode in photoelectrochemical water splitting would be to use nanostructures like nanowires, nanowire networks or nanocubes [31]. Especially for Cu$_2$O with a diffusion length of minority charge carriers (electrons in the case of p-Cu$_2$O) of only 20–100 nm, and an absorption depth near the bandgap of approximately 10 µm [16,32–34], the use of one-dimensional

![Fig. 7. Energy band diagram of p-Cu$_2$O films including the redox potentials for all reactions taking place during the photoelectrochemical experiments as described above (Reactions (5)-(14)). The reactions in blue are taking place without H$_2$O$_2$ added to the electrolyte solution, the reactions in red take place when H$_2$O$_2$ is added as an electron scavenger, and the reactions in black are either not considered or only taking place at the start of the measurement until the Cu$_2$O reduction reaction takes over (for interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).](image-url)
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 photoreduction 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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