Preparation and optimization of transparent cuprous oxide photocathodes for allowing efficient solar water splitting

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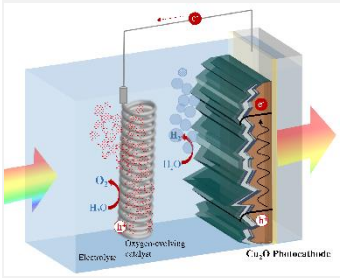

Efficient solar-to-hydrogen energy conversion is anticipated to be an emerging process in a future sustainable energy economy. Photocathodes based on Cu_2O are promising materials for large scale H_2 generation but an external bias is necessary due to its unfavorable band edge alignment with the electrolyte. A tandem arrangement by combining two or more semiconductors should attain unassisted water splitting and the development of a transparent material is a requisite. Thus, a highly active and stable transparent photocathode was developed comprising p-type Cu_2O and n-type nanolayers of Al-doped ZnO (AZO) and TiO_2, activated with RuO_2 co-catalyst. Photocurrents of about 5 $mA \cdot cm^{-2}$ and 2 $mA \cdot cm^{-2}$ were observed for front and backside illumination at 0 V_{RHE}, respectively. Only a 10 % loss occurred after 20 hours under visible light irradiation. In a tandem PEC cell, a conversion efficiency greater than 6 % is expected.

Introduction

Solar energy is one of the most important natural sources of renewable energy. With around 120 PW of solar energy continuously hitting the earth surface, it seems to be a viable alternative to overcome the current global energy demand.[1] The production of solar fuels is a promising route and, in particular, hydrogen generated via photoelectrochemical (PEC) water splitting.[2] PEC water splitting cells integrate collection of sunlight and water electrolysis in a single device to further produce hydrogen and oxygen (O_2).

Numerous semiconductor materials and PEC device configurations have been investigated for several decades, since the pioneering work of PEC water cleavage using a photoanode of TiO_2 by Fujishima and Honda in 1972.[3] The requirements on the semiconductor materials are strict: suitable bandgap to cover water dissociation (1.23 eV), harvest a significant portion of the solar spectrum, favorable band edge positions to enable both water reduction and oxidation, as well as practical durability and low-cost. Moreover, the minimum bandgap should be at least 1.9 eV as a result of thermodynamic losses and the required overpotentials for fast reaction kinetics.[4] Despite the research efforts to date, no single semiconducting material has been found that fulfill all these constraints. In most cases, an external bias is necessary to generate solar hydrogen from water splitting due to non-ideal band edge alignment of the semiconductor with the electrolyte and/or insufficient charge separation (smaller photovoltage). Nevertheless, the ideal PEC cell should work without any external bias and a combination of two or more semiconductors in a tandem arrangement may offer an attracting solution.[5,6] In addition, the combination of stable and inexpensive metal oxide semiconductor materials in a tandem approach can offer an elegant and economic route for solar H_2 production. For a stacked configuration tandem cell, the development of a transparent photoelectrode is needed since the portion of solar radiation that is not absorbed by the semiconductor can be transmitted and converted by the second photosystem (*e.g.* an n-type photoanode or a PV device), improving the efficiency of the system.

Recently, p-type photocathode materials for water reduction started to become popular with the development of nanostructuring and protection techniques. Cuprous oxide (Cu_2O) materials exhibiting a bandgap energy of 2.0 – 2.2 eV has a great potential for solar hydrogen production, but their poor stability in aqueous solutions is the main limiting factor for using them in water reduction.[7] However, the use of protective ultrathin overlayers of AZO and TiO_2 facilitate the charge extraction and suppress the corrosion, making this electrode the state-of-the-art p-type oxide.[8,9] Despite the recent success with this structure, the Cu_2O thin films are deposited on top of an opaque Au-coated layer over the FTO substrates to obtain better deposition reproducibility. The present work studies a highly active and stable transparent Cu_2O photocathode with a protective layer and activated with RuO_2 co-catalyst. In addition, the onset potential and the fill factor were improved since high photocurrents at low reverse potentials are more interesting for tandem approaches.

Methods

Cuprous Oxide photocathode preparation

The working electrodes of cuprous oxide thin films were electrodeposited from a basic solution of lactate-stabilized copper sulphate over fluorine-doped tin oxide (FTO) glass substrates coated with gold, as reported elsewhere.[8,9] The thickness of the Au over coating layer (OCL) deposited by thermal evaporation was varied among 150 nm for the standard photocathodes[10] and 1 nm, 3 nm and 5 nm for the transparent photocathodes. Moreover, the time of electrodeposition was also varied to study the effect of Cu_2O thickness on the transparency of the film: 105 minutes, 50 min and 25 min, being achieved films of around 650 nm, 330 nm and 160 nm, respectively.

To protect these films concerning photocathodic decomposition in water, ultrathin n-type oxides overlayers were deposited atop the Cu_2O films. The deposition was carried out using thermal ALD systems, as described previously.[10] Finally, RuOx co-catalyst was galvanostatically deposited using an aqueous solution of 1.3 mM $KRuO_4$, at a current density of -28.3 μA cm^{-2} for 15 min under simulated one sun illumination.[10]

Photoelectrochemical measurements

The PEC cell performance was evaluated in a standard three-electrode configuration using the Cu_2O electrode as photocathode, Pt wire as counter-electrode and a reference electrode of Ag/AgCl/Sat. KCl. The electrolyte solution was 0.5 M Na_2SO_4 buffered with 0.1 M phosphate to obtain pH 5.0. The Ivium Potentiostat/Galvanostat was used to acquire the photoresponse under chopped irradiation from a 450 W Xe-lamp equipped with an IR/UV filter, calibrated with a silicon diode to simulate AM 1.5 illumination (100 $mW \cdot cm^{-2}$). The scan rate for current-voltage (*J-V*) curves was 10 $mV \cdot s^{-1}$ in the cathodic direction.

Results and Discussion

Figure 1 shows the *J-V* curves of the Cu_2O photocathodes deposited over different thicknesses of Au layers (150 nm[10], 3 nm and without Au).

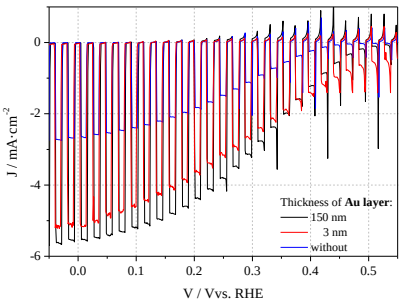

Figure 1. *J-V* characteristics of the Cu_2O photocathodes with different Au OCL thicknesses under light chopping.

The Cu_2O electrode deposited with the reference conditions shows a plateau photocurrent around 5.5 $mA \cdot cm^{-2}$ at 0 V *vs* the reversible hydrogen electrode (RHE), similar to results reported elsewhere[10]. The sample without gold shows a current density decrease of *ca.* 50 % and a later onset potential. On the other hand, the Cu_2O film deposited on top of 3 nm Au OCL presents a slightly higher onset potential, but the current decreases to *ca.* 5.2 $mA \cdot cm^{-2}$ at 0 V_{RHE}. The gold OCL seems to create an important adhesion layer with the active Cu_2O film, playing a crucial role to increase the conductivity and the PEC performance. Regarding this evidence, the relation between the Au OCL thicknesses and the Cu_2O electrodeposition time on the behavior of the photocathodes was studied.

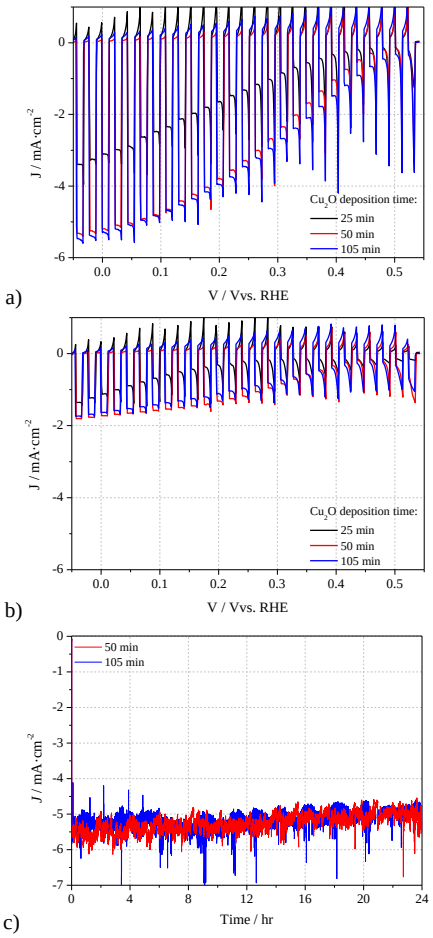

Figure 2. *J-V* characteristics of the Cu_2O photocathodes prepared by varying the electrodeposited time atop the 3 nm of Au OCL. The tests were performed under light chopping in: **a)** front side and **b)** backside illumination. **c)** Stability test of the Cu_2O photocathodes (105 min and 50 min), biased at 0 V_{RHE} under continuous light.

Error! Reference source not found.a and b show the *J-V* characteristics of the Cu_2O photocathodes electrodeposited for 105 min, 50 min and 25 min on top of 3 nm Au-coated FTO substrates, illuminated from the front and backside, respectively. From **Error! Reference source not found.**a the decrease of the deposition time to half did not affect the plateau current and photocurrents higher than 5.2 $mA \cdot cm^{-2}$ at 0 V_{RHE} were observed for both materials, whereas decreasing the standard time to 25 minutes sacrificed the efficiency (3.1 $mA \cdot cm^{-2}$). However, the onset potential and the fill factor are worse with thinner Cu_2O films, *i.e.*, a current decrease of 15 % at 0.4 V_{RHE} is observed with the photocathodes deposited for 50 min. By illuminating the photocathode from the backside (**Error! Reference source not found.**b), the onset potential was similar for all samples, but the plateau photocurrent increased from 1.6 to 1.8 $mA \cdot cm^{-2}$ by reducing the standard thickness of the films by half and it decreased to 1.2 $mA \cdot cm^{-2}$ by reducing the thickness to 1/4. **Error! Reference source not found.**c shows the stability of the most promising materials; they are stable against corrosion for more than 1 day of continuous illumination when biasing at 0 V_{RHE}. The standard Cu_2O film with 650 nm deposited atop a 3 nm Au OCL FTO-glass showed only 10 % loss after 20 hours of testing, which corresponds to a great stability enhancement over the non-transparent materials (with 150 nm of Au OCL) reported recently.[10] The photocathodes with a Cu_2O film of 330 nm showed no losses after 8 h and only a 10 % loss after 24 hours.

In an effort to understand the effect of the Au OCL over FTO substrates on the performance of the standard photocathodes, the thickness of the Au-coated layer was also varied among 1 nm, 3 nm and 5 nm and the corresponding *J-V* curves are presented in Figure 3. Thus, plateau photocurrents of around 5.1 – 5.5 $mA \cdot cm^{-2}$ at 0 V_{RHE} are observed for the different samples; however, the onset potential is shifted to more positive values and the fill factor is strongly enhanced as the Au OCL thickness increases. H_2 generation starts at potentials higher than +0.55 V_{RHE} with the film deposited atop a 5 nm Au-coated FTO substrate and the improved fill factor enabled photocurrents of *ca.* 3 $mA \cdot cm^{-2}$ at +0.4 V_{RHE}. This fill factor is even better than the one achieved with the standard photocathode (around 2 $mA \cdot cm^{-2}$ at +0.4 V_{RHE}). It is clear that the FTO-glasses with 5 nm Au layer allows to improve the onset potential and efficiency of the photocathodes, which is really promising for tandem cell applications.

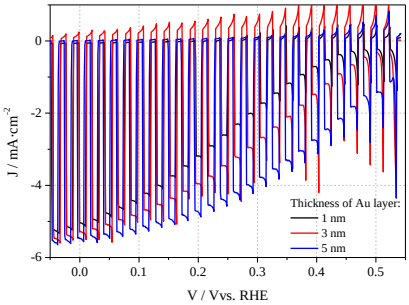

Figure 3. *J-V* characteristics of the standard Cu_2O photocathodes (105 min) electrodeposited atop Au OCL with different thicknesses, biased at 0 V_{RHE}. The tests were performed under light chopping in front-side illumination.

Conclusions

An efficient transparent Cu_2O photocathode was developed, remaining stable after 1 day under continuous light. This material can work in a tandem configuration with a DSC to allow unassisted water splitting. The photocurrent of *ca.* 5 $mA \cdot cm^{-2}$ obtained with this electrode would correspond to a solar-to-hydrogen conversion efficiency greater than 6 % in a tandem PEC cell. Further research is needed to increase the performance of the system, namely by improving the onset potential and the plateau photocurrent of the Cu_2O film with nanostructuring and catalysis studies.

Acknowledgements

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