Cu_2O: a catalyst for the photochemical decomposition of water?

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The photoelectrochemical properties of polycrystalline Cu_2O electrodes are discussed with regard to the application of the oxide as a photocatalytic material for water splitting.

Recently, illuminated Cu_2O was reported to act as a stable catalyst for water splitting. Hydrogen and oxygen were evolved in a vigorously stirred suspension of Cu_2O particles, without a noticeable decrease in activity over a period of 1900 h.[1] This was very surprising since single crystalline Cu_2O is known to be photocathodically unstable.[2] The mechanism of water splitting and the precise role of the Cu_2O are still unclear.[1,3] Photocatalysis at a p-type semiconductor such as Cu_2O implies that the majority charge carriers (holes) oxidize water to oxygen, while the photogenerated minority charge carriers (electrons) reduce water to hydrogen. These reactions can be studied electrochemically; at positive potentials an anodic dark current due to oxygen evolution is expected, and at negative potentials a cathodic photocurrent accompanied by hydrogen evolution. We were already involved in research on electrodeposited polycrystalline Cu_2O layers,[4] and decided to study the photoelectrochemistry of these layers with respect to the decomposition of water.

We prepared well defined Cu_2O consisting of 0.1–1 μm crystals on a transparent, fluorine-doped tin oxide substrate by reduction of Cu^{2+} from a saturated copper(II) lactate aqueous solution. This technique has been described elsewhere.[4–8] Films were grown galvanostatically at 55 °C and pH 11 at a current density of 0.2 mA cm^{-2}. In the X-ray diffraction spectra only peaks due to Cu_2O were found. A bandgap of 1.9 eV was estimated from the optical absorption, in good agreement with literature values. Absorption at wavelengths > 600 nm due to CuO was not seen. Scanning electron microscopy showed only well defined crystals. No changes in appearance or photoelectrochemical properties were found on keeping the Cu_2O layers in air for months.

The photoelectrochemical properties were investigated using a three electrode set-up with 0.5 M Na_2SO_4 as electrolyte solution. This method has the advantage that the cathodic and anodic reactions on the Cu_2O working electrode can be studied separately; they are accompanied by the reduction or oxidation of water at the platinum counter electrode. In the dark an anodic current, corresponding to the oxidation of the Cu_2O [eqn. (1)], was observed at potentials above 0.0 V *vs.* SCE (all redox potentials[9] are *vs.* SCE and at pH 7):

$$Cu_2O + 2\ OH^- + 2h^+ \rightarrow 2\ CuO + H_2O \quad E = -0.05\ V \quad (1)$$

The CuO slowly dissolves. In the presence of oxygen, a small steady state dark current was observed at negative potentials. When the solution was thoroughly purged with argon this dark current could be reduced to < 1 μA cm^{-2}.

Under illumination, a large cathodic photocurrent was observed with an air-saturated solution under strong convection. This photocurrent started at a potential between 0.0 and 0.1 V, and the photocurrent spectrum was in good agreement with the Cu_2O absorption spectrum. Fig. 1(a) shows the current at −0.4 V *vs.* SCE under chopped 350 nm illumination. At low light intensities the photocurrent increased linearly with increasing photon flux; quantum efficiencies of 50% were measured for a photon flux below $5 \times 10^{14}\ s^{-1}\ cm^{-2}$. At higher light intensities

Fig. 1 Current density at −0.4 V measured on a 0.5 μm thick Cu_2O electrode illuminated with 350 nm ($5 \times 10^{15}\ s^{-1}\ cm^{-2}$) in 0.5 M Na_2SO_4 solution: (a) bubbled with air, (b) bubbled with Ar and (c) bubbled with Ar and with 40 mM MV^{2+} added to the solution.

the photocurrent levels off. When the solution was carefully purged with argon, the cathodic photocurrent was very low (≈ 1 μA cm^{-2}) as is shown in Fig. 1(b). It is clear that the current observed in air-saturated solution is due to oxygen reduction, for instance *via* eqn. (2).

$$O_2 + 2\ H_2O + 2e^- \rightarrow H_2O_2 + 2\ OH^- \quad E = +0.03\ V \quad (2)$$

The hydrogen peroxide is further reduced to water. The high intensity photocurrent limit was close to the limiting current density for oxygen reduction at a platinized indium tin oxide electrode under the same hydrodynamic conditions. Obviously, the photocathodic reduction of oxygen on Cu_2O is extremely efficient. On the other hand, the reduction of water to hydrogen seems negligible. If appropriate deposition conditions were used, the Cu_2O layers, in contrast to single crystalline electrodes,[2] proved to be surprisingly stable under photocathodic conditions. The photocurrent due to oxygen reduction was constant over long periods, even when the photon flux exceeded the oxygen flux to the electrode surface. No evidence was found for the formation of copper due to the reduction of Cu_2O (E = −0.19 V). The small photocurrent observed in argon-purged solutions is very likely due to the reduction of traces of oxygen left in the solution.

The methylviologen (1,1-dimethyl-4,4-bipyridinium) system, $MV^{2+}/MV^{\cdot+}$ has a redox potential of −0.60 V *vs.* SCE,[10] which is close that of hydrogen. Fig. 1(c) shows a photocurrent transient for an Ar purged 0.5 M Na_2SO_4 solution containing 40 mM $[MV]Cl_2$. In the absence of oxygen, the photocurrent quantum efficiency was initially very high. However, the photocurrent decreased rapidly with time. This is likely due to the formation of a MV^0 layer on the electrode surface. The $MV^{\cdot+}$ radical cation, which is formed upon reduction of MV^{2+}, can be further reduced to MV^0; redox potentials of −1.1 to −1.3 V are reported for this reaction.[10–12] MV^0 is not soluble in aqueous solutions and is known to form blocking films on the electrode surface.[13] This is in good agreement with the observation that the photocurrent is restored as soon as air is admitted to the cell. Oxygen is known to oxidize MV^0 to MV^{2+} very effectively. Obviously the kinetics for the reduction of MV^{2+} are much more efficient than those for the reduction of water.

Fig. 2 Overview of the redox potentials of the relevant reactions with respect to the estimated position of the Cu_2O band edges.

It is interesting, in the light of our results, to examine the requirements that have to be met if Cu_2O is to function as a photocatalyst for water splitting. It is crucial that both the reduction and oxidation reactions of water are thermodynamically possible, and that these reactions are kinetically favourable. Fig. 2 shows the redox potentials of the relevant reactions with respect to the positions of the Cu_2O band edges.[2] To reduce water, the electron Fermi level and hence also the conduction band edge must be at an energy higher than that corresponding to the reduction potential for water, which at pH 7 is −0.65 V. The estimated position of the edge of the Cu_2O conduction band is −1.4 V.[2] This means that a large overpotential is available for the reaction. However, our measurements show that in the absence of other redox species no significant cathodic photocurrent is found in aqueous electrolyte. In the presence of oxygen or the methylviologen cation very efficient photocathodic reactions were found. The reduction of water must be kinetically highly unfavourable at our illuminated Cu_2O. To enable the oxidation of water, the Cu_2O valence band edge must be at an energy below that corresponding to the oxidation potential of water, which at pH 7 is *ca.* +0.57 V. The edge of the valence band was estimated to be at +0.6 V.[2] It is unlikely that the valence band edge lies at a much lower energy. This can be deduced from the bandgap of 2 eV and the fact that the position of the conduction band edge must be significantly more negative than −1.2 V *vs.* SCE if the photocathodic reduction of $MV^{\cdot+}$ (E = −1.2 V *vs.* SCE) is to be possible. As a consequence (almost) no overpotential is available for the oxidation of water. Furthermore, the oxidation of Cu_2O, with a redox potential of −0.05 V, is thermodynamically considerably more favourable. Our results show that the anodic current in the dark corresponds at least partly to oxidation of the oxide. Therefore, although the Cu_2O is stable under photocathodic conditions, stability under open circuit illumination is unlikely.

On the basis of these results it seems questionable if water can be split at Cu_2O *via* a normal photocatalytic reaction. However, our polycrystalline layers show long term stability under photocathodic conditions, and a surprisingly high quantum efficiency for the photocathodic reduction of both oxygen and the methylviologen cation. Therefore Cu_2O could be a promising material, not for direct photoelectrochemical water splitting, but in conjunction with a suitable redox system as a p-type photoelectrode in an electrochemical photovoltaic cell.

Notes and references

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