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Electrical Properties of Cu₂O Films Prepared by Electro-Deposition Method

In this work, the electrical properties of electrodeposited Cu₂O in aqueous solutions were investigated. The results explained good stability under illumination conditions at negative potentials. The diffusion length of electrons in the sample was determined to be about 10-100nm. The deposited Cu₂O films could be a promising material in electrochemical photovoltaic cells technology.

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1. Introduction

Cuprous oxide as a material for the conversion of solar energy into electrical or chemical energy has received relatively little attention. Several papers have considered the use of the material in a solid-state photovoltaic cell, such as Schottky barrier device obtained by applying metal contacts to the Cu₂O. The oxide is very easily reduced and in all cases, a copper rich phase formed near the Cu₂O/metal interface [1-3].

Another option would be to use the material in a photoelectrochemical (PEC) cell. A problem might be the limited stability of Cu₂O in aqueous solutions. Cu₂O is stable only in a limited pH range [4]. The redox potentials for the reduction and oxidation of the monovalent copper oxide lie well within the band-gap, making possible the decomposition reactions by photogenerated electrons or holes thermodynamically [5]. Furthermore, single crystalline Cu₂O is being reduced to copper under photocathodic conditions [6]. However, a paper was published [7] indicating that illuminated Cu₂O particles could show good stability while acting as a catalyst for water splitting. Hydrogen and oxygen were evolved in a rapidly stirred, illuminated suspension of millimeter-sized particles, without a noticeable decrease in activity for a period over 1900 hours.

A second paper was published later in which the water splitting was found to continue for many hours after the light was turned off. The authors tried to explain their results by proposing that the mechanical energy supplied by the stirring was converted into chemical energy, with the oxide acting as a catalyst [8].

In this paper, we study the electrical and chemical properties of Cu₂O deposited in aqueous solutions. The photocathodic reduction reactions of oxygen and the 1,1-dimethyl-4,4-

bipyridinium cation (methylviologen, MV21) will be described. We will consider the decomposition reactions of Cu₂O in aqueous environment and its potential for direct photochemical water splitting or use in a PEC solar cell.

2. Experiment

Cu₂O was deposited on transparent, fluorine-doped SnO substrates by reduction of Cu²⁺ from a saturated Cu(II) lactate solution. Layers with a thickness up to ~10μm could be grown with a deposition efficiency of about 0.9. This deposition efficiency was determined by measuring the charge for deposition and subsequent anodic dissolution. The layer thickness was determined from the interference patterns in the absorption spectra. The Cu₂O used in the present work was grown at pH 11 and 558°C, with a current density of 0.2mA/cm². A band-gap of 2.0eV was estimated from the optical absorption, in good agreement with literature values. Due to CuO, we did not observe absorption at wavelengths longer than 600nm. The electrical and chemical properties of the Cu₂O layers did not change for months despite they were kept in air.

The measurements were performed in a three electrode setup, using a potentiostat, a large area platinum counter electrode and a saturated calomel reference electrode (SCE). The aqueous electrolyte solutions contained 0.5M Na₂SO₄ or 40mM MVCl₂ in 0.5M Na₂SO₄, and were bubbled with either air or argon.

3. Results and Discussion

Fig. (1) shows the I-V characteristics of a 0.5μm thick Cu₂O electrode in 0.5M Na₂SO₄ solution in the dark. At potentials above 0.0V an anodic current was observed, corresponding to the oxidation of the Cu₂O (all redox potentials

mentioned in this paper are vs. SCE, refer to pH 7 and were taken from [10]):

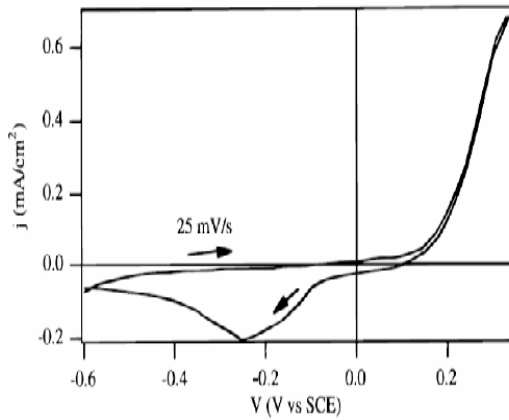
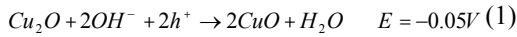
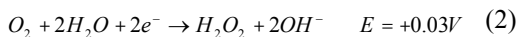


Fig. (1) I-V characteristics of a 500nm thick Cu₂O layer in 0.5M Na₂SO₄ aqueous solution

In a Na₂SO₄ aqueous solution the CuO slowly dissolves. The CuO can be partly reduced by scanning back to negative potentials. In the presence of oxygen, a small steady-state cathodic current was observed. When the argon was sluiced through solution, this dark current could be reduced to less than 1μA/cm². At potentials more negative than -0.6V vs. SCE a fast increasing cathodic current was found due to the reduction of the oxide to copper.

Under illumination, a large cathodic photocurrent was observed with an air-saturated solution under strong convection. When the argon was carefully sluiced through solution, the cathodic photocurrent was very low (~1μA/cm²). It is clear that the photocurrent observed in air-saturated solution is due to oxygen reduction:



The hydrogen peroxide is very likely reduced further to water [11]. The reduction of oxygen to hydrogen peroxide has been studied for instance at illuminated p-GaAs, GaP and n-type and p-type InP [12-14]. It is a multistep reaction involving a HO₂ intermediate. Current doubling was observed at low light intensities, as the HO₂ intermediate could inject a hole into valence band.

Fig. (2) shows the I-V characteristics for a 0.5μm thick Cu₂O electrode under chopped illumination at 350nm. The photocurrent (I_{ph}) starts at a potential between 0.0 and 0.1V and increases continuously with decreasing potential. Obviously, the photocathodic reduction of oxygen on Cu₂O is extremely efficient. The photocurrent was constant over long periods,

even when photon flux exceeded the oxygen flux to electrode surface.

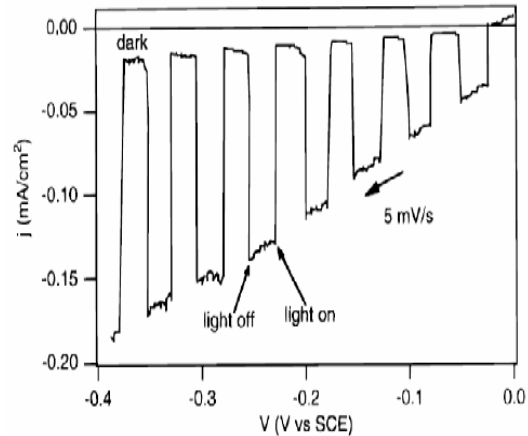


Fig. (2) I-V characteristics for a 500nm thick Cu₂O layer under chopped 350nm illumination in 0.5M Na₂SO₄ solution bubbled with air

Fig. (3) shows the I-V characteristics for a 0.5μm thick Cu₂O electrode in a 0.5M Na₂SO₄ aqueous solution bubbled with air in the presence of MV²⁺. The photocurrent quantum efficiency at -0.4V vs. SCE was 0.2. The photocurrent decreased continuously with time. The current decayed to 50% of its initial value after the passage of about 12mC/cm². The photocathodic current has partly recovered after a period in the dark.

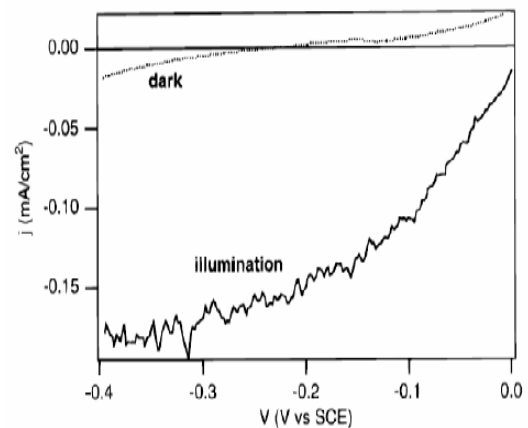


Fig. (3) I-V characteristics for a 500nm thick Cu₂O layer in the dark and under 350nm illumination. Electrolyte is 10mM MV²⁺ in 0.5M Na₂SO₄ solution bubbled with air

4. Conclusions

The properties of deposited Cu₂O were investigated. In the dark the oxide dissolves at potentials above 0.0V. A small cathodic dark current can be found due to the reduction of oxygen. In contrast to single crystalline Cu₂O, these deposited layers were stable under illumination. High efficiencies were found for the photocathodic reduction of oxygen and the

methylviologen cation. The diffusion length of minority charge carriers (electrons in the conduction band) is in the range of 10-100nm. No evidence was found for the reduction of water. Based on our results, it seems unlikely that water can be split photochemically at Cu_2O .

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