# Electrochemical and Photoelectrochemical Properties of $Cu_2O$ Electrode in Aqueous Solutions

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## Introduction

Cuprous oxide ($Cu_2O$) is one of promising materials because it is a p-type semiconductor with a band gap of 2 eV suitable for solar energy conversion, and is also inexpensive and harmless. The problem of $Cu_2O$ lies in low stability under illumination. The redox potential for the reduction ($Cu_2O$/Cu) exists within its band gap, and thus $Cu_2O$ is predicted theoretically to be easily reduced to Cu by photoexcited electrons.[1]

Nagasbramanian *et al.* reported that $Cu_2O$ was stable in an aprotic organic solvent (acetonitrile) containing a redox couple.[2] Recently Hara *et al.* reported that $Cu_2O$ particles were stable even in aqueous solutions showing water splitting.[3] The finding was later correlated with the mechanochemical properties of $Cu_2O$.[4] In relation to this findings, de Jongh *et al.* investigated the photoelectrochemical properties of electrodeposited $Cu_2O$ electrodes.[5] They showed the fundamental properties of $Cu_2O$ as a photoelectrode in an aqueous solution. $Cu_2O$ was used as a photoelectrode which can reduce methylviologen (2+/0) which redox potential is more negative. Although the long term stability under illumination was proved at certain potential region, the degradation process was not clearly shown.

On the other hand, one of the authors S. Kuwabata *et al.* reported that electrochemical reduction peaks for intermingled copper oxide ($Cu_2O$ and CuO) films prepared on copper plates by thermal oxidation were shifted to far more negative potentials in strong alkaline solutions containing $Li^+$ ion (6M KOH + 1M LiOH), compared with the absence of $Li^+$ ions.[6] The result suggests that a new possibility of the stabilization of $Cu_2O$ by control of electrolyte composition.

In the present work, we investigated the electrochemical and photoelecrochemical properties of $Cu_2O$ electrodes in various aqueous solutions of varied pH to clarify the stability.

## Experimental

$Cu_2O$ electrodes was prepared by the method of electrodeposition according to the procedure reported by Bohannan *et al.*[7] Electrochemical measurements were carried out using a conventional three-electrode cell with Ag|AgCl as the reference electrode and Pt plate as the counter electrode. Light source is a 300W Xe lamp with cut-off filters for UV (<350nm) and IR (>800nm) light. Electrochemical measurement was done by voltammetry for the reduction of $Cu_2O$ electrode in 6M KOH + 1MLiOH. Photocurrent measurement was done in the solution saturated dissolved oxygen at a fixed potential for 1h under illumination modulated with a light chopper. The properties of $Cu_2O$ electrodes were investigated by electrochemical reduction, X-ray diffraction and ESCA analysis.

## Result

Figure 1 shows the chronoamperograms in 1M LiCl at a potential under illumination of 0.4Hz. Stable photocurrent due to reduction of dissolved oxygen was observed at -0.4V for 1h. This potential is more negative potential than the standard redox potential for $Cu_2O$/Cu (Equation (1)).

$$Cu_2O+H_2O+2e^- \rightarrow 2Cu+2OH^- \quad E^0 = -0.562\ \text{V vs. Ag|AgCl} \quad \cdots (1)$$

The photocurrent efficiency in a neutral solution was higher than that in an alkaline solution. The photocurrent was stable for more than 60 min when the electrode potential was kept at –0.4 V, but not in more negative potentials.

Figure 2 shows the voltammograms of the $Cu_2O$ electrode before and after the experiment in Figure 1. Comparable reduction current from $Cu_2O$ to Cu was observed at the electrode after the experiment. This result suggests that $Cu_2O$ was hardly reduced at -0.4V and even under illumination. The results proved that the photoelectrochemical degradation of $Cu_2O$ can be suppressed under appropriate potentials in neutral solutions.

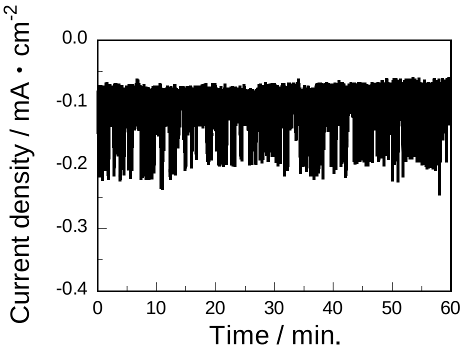

Figure 1. Chronoamperogram of the $Cu_2O$ electrode in $O_2$-saturated 1M LiCl aq at -0.4V under illumination of 0.4Hz

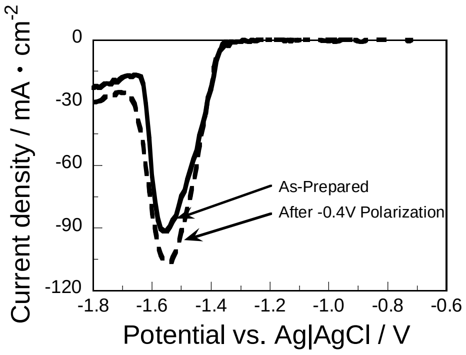

Figure 2. Voltammograms of the $Cu_2O$ electrode before and after the photoelectrochemical experiment, measured in 6M KOH + 1M LiOH aq.

## References

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