Potentiostatic Electrodeposition of Cu_2O under Light and Dark for Photoelectrochemical Hydrogen Generation Applications

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Abstract. *Potentiostatic electrodeposition conducted at various deposition voltages from lactate-stabilized copper sulfate electrolyte was used for preparation of Cu_2O layers for Photoelectrochemical (PEC) production of hydrogen. A novel approach based on an application of light during the electrodeposition is utilized to suppress the potential drop in the Cu_2O layer during the potentiostatic deposition. Structures prepared under dark and light on an Ag substrate are analyzed by X-Ray Diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Linear Sweep Voltammetry (LSV). It was shown that the application of light increases the deposition rate due to the contribution of the photogenerated carriers. The deposition voltage affects the photoresponse of light deposited structures but causes only a negligible change in dark deposited structures. The light deposited samples exhibited a higher photoresponse for all deposition voltages. The presented study suggests the light potentiostatic electrodeposition as an attractive approach for the preparation of Cu_2O structures for cheap and efficient photoelectrochemical water splitting applications.*

Keywords

Cu_2O, electrodeposition under light, hydrogen, XRD, water splitting.

1. Introduction

The possibility to prepare hydrogen by water splitting under illumination presents an appealing approach for the conversion of solar light into a good usable energy source [1] and [2]. Materials with a high energy conversion efficiency and cheap fabrication processes are of demand to make this new approach for energy conversion industrially attractive. Cuprous oxide (Cu_2O) with a bandgap of $\sim$ 2.1 eV and possible preparation by electrodeposition [3] is an attractive candidate for cheap Photoelectrochemical (PEC) electrodes. Copper cation vacancies present in Cu_2O are responsible for p-type conductivity [4], which predetermines Cu_2O as a photocathode for Hydrogen Evolution Reaction (HER). To achieve a high rate of HER, the photocurrent is one of the most important parameters. The photocurrent of 2.4 mA·cm^{-2} was achieved on the single Cu_2O layer forming simply PEC cell [5]. A significant increase of the photoresponse to 7.6 mA·cm^{-2} can be achieved by preparing additional layers TiO_2, ZnO, and RuO_2 on a Cu_2O forming PN junction and providing corrosive protection and higher catalytic efficiency [6].

The electrodeposition provides numerous advantages which include: (1) simple and inexpensive equipment; (2) short time of deposition; (3) uniform and homogeneous layers; and (4) cheap and scalable process [7]. The electrodeposition conditions such as applied potential, pH and temperature have a strong influence on the morphology and crystalline properties and determine the photoelectrical properties of the Cu_2O layers [8] and [9].

Two modes of electrodeposition are frequently used for the preparation of Cu_2O, i) deposition with fixed current (galvanostatic deposition) and ii) deposition with fixed potential (potentiostatic deposition). The main drawback of the galvanostatic electrodeposition is low control over the nucleation and deposition of the initial layer on a substrate. The main limitation of the potentiostatic deposition is on the other hand decrease of the deposition potential at the surface of the deposited layer. This is due to the potential drop in the layer due to the increased thickness and resistivity of the layer. A recent study revealed higher photoresponse for the potentiostatic electrodeposition [10].

In this paper, we analyze the Cu_2O structures prepared by a potentiostatic electrodeposition at various deposition voltage. A new approach based on the application of light during the electrodeposition was introduced within this study. The light, which is absorbed in the Cu_2O, can increase the conductivity of the deposited layer and thus have the ability to suppress the decrease of the deposition potential at the Cu_2O surface. While the bandgap of Cu_2O is around 2.1 eV, only light with wavelength below 590 nm is absorbed. The X-Ray Diffraction analysis (XRD), Scanning Electron Microscopy (SEM) and Linear Sweep Voltammetry (LSV) of the electrodeposited samples are provided to gain an insight on the influence of the light and deposition voltage on the properties of the Cu_2O layers.

2. Experimental

The p-type Cu_2O thin films were electrodeposited on ITO and Ag coated glass by AUTOLAB PGSTAT128N potentiostat. A three-electrode configuration was used with Pt as a counter electrode, saturated Ag/AgCl reference electrode and the substrate as a working electrode to control the deposition conditions carefully in the potentiostatic mode. Copper (II) sulfate ($CuSO_4$, 0.4 mol/L) and L-lactic acid (3 mol/L) were used as an electrolyte. The LiOH was used to adjust the pH of the electrolyte to 12.4. All used chemicals were obtained from Sigma Aldrich. All depositions were carried out at deposition voltages $V_d = -350$, -400, -500 and -600 mV vs. Ag/AgCl (denoted as V_d in the sequel) and deposition temperature 45 °C controlled by a water bath. All samples were prepared with area 1 cm^2. The deposition time was set to 1800 s. Deposition on Ag substrate was carried out under dark and light. A Light-Emitting Diode (LED) lamp with the light intensity of 2000 $W{\cdot}m^{-2}$, measured by a silicon calibration solar cell, was used as a source of light during the deposition. The LED lamp with warm white illumination spectrum was used to provide sufficient light with the wavelength below 590 nm to be absorbed in the Cu_2O. XRD analysis was conducted by Bruker D8 Advance diffractometer equipped with a Cu anode operating at 1.6 kW. SEM analysis was provided by LEO 1550. The thickness of the structures was measured by profilometer Dektak 150.

The photoelectrochemical characterization was carried out by Linear Sweep Voltammetry (LSV) in a three-electrode mode with a Pt counter electrode and a saturated Ag/AgCl reference electrode by using the potentiostat AUTOLAB PGSTAT128N. A sweep rate of 10 $mV{\cdot}s^{-1}$ was used during the LSV measurements. The electrolyte was 0.5 M Na_2SO_4 with pH 6.4. The potential of LSV measured data was calculated versus a Reversible Hydrogen Electrode (RHE). A solar simulator with the light intensity of 1000 $W{\cdot}m^{-2}$ and spectrum AM 1.5 was used as a source of light. The light was chopped with a frequency ∼100 mHz to simultaneously study the light and dark behaviour of the samples during the measurements.

3. Results and Discussion

Figure 1 shows the deposition current I_d measured during 1800 seconds of the potentiostatic electrodeposition of Cu_2O samples under dark (solid line) and light (dashed line) at $V_d = -350$, -400, -500 and -600 mV. All V_d are considered vs. Ag/AgCl reference electrode. The deposition process can be divided into two phases shown in Fig. 1. The first phase is characterized by a high current density for all light and dark deposited samples. During this phase, the electrolyte is in contact with the Ag substrate and the Cu_2O nucleation and growth of the initial layer at the substrate is carried out. The strong decrease of Id is associated with the increased coverage of Ag by Cu_2O and increased resistive losses. The similar I_d behaviour for light and dark deposited samples indicates that light has a negligible

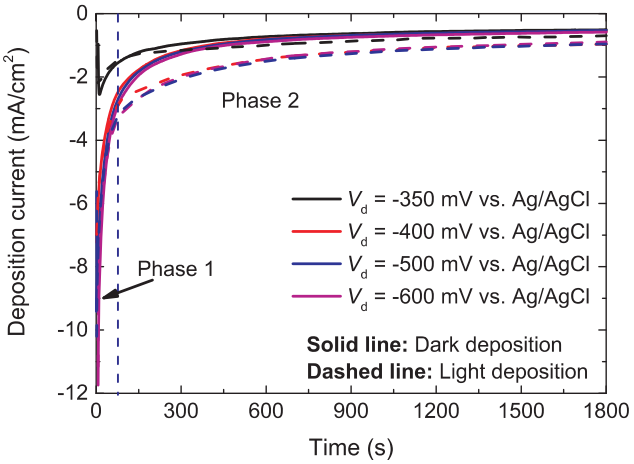

Fig. 1: Deposition current for samples deposited under dark and light at different V_d.

influence on the nucleation in this phase of growth. The higher I_d upon the cathode increase of V_d reflects a higher nucleation rate at higher deposition voltages and is observed for both light and dark deposited samples. The second growth phase is characterized by a slow decrease of I_d. The full Cu_2O coverage of the substrate and increased resistive losses are expected in this phase of deposition. The slow saturation of I_d has its origin in the increased resistive losses at the thicker Cu_2O during the growth. A higher I_d is shown for all light deposited samples in this second growth phase. The absorbed light in the Cu_2O causes photogeneration of electron-hole pairs, which decreases the resistance of the layer and contributes to the reduction of the electrolyte whereby, increasing the deposition rate. In this way, the application of light during the deposition has the ability to partially suppress the decrease of the deposition voltage at the surface, which is caused due to the resistive losses in the Cu_2O layer.

The photogenerated current contributes to the growth of the layer, thus higher thicknesses are expected for light deposited samples. The thickness of the layer is directly related with the deposition charge, which passed through the electrolyte during the deposition process. Such charge is calculated by integration of the deposition current vs. time. Higher deposition charge is expected for the light deposited sample. Figure 2 shows the thickness and deposition charge of the prepared Cu_2O layers deposited under dark and light at different V_d. All light deposited samples exhibited higher thicknesses and charges compared to dark deposited samples. This confirms the above assumption and indicates a higher growth rate of Cu_2O layer under the light. The electrodeposition is determined by the reduction of the electrolyte, which is nonlinear voltage dependent mechanism. Because of this, the relationship between V_d and thickness is also not linear. For dark deposited samples, the thickness and deposition charge of Cu_2O layers increase with the deposition voltage. The higher cathode V_d partially compensates the potential drop in the Cu_2O layer caused by resistive losses, leading to a higher I_d and higher layer thicknesses. In the case of light deposited samples, the thicknesses of the prepared Cu_2O exhibit the maximum at -500 mV and decrease with an increase of V_d to -600 mV vs. Ag/AgCl. The difference between thicknesses and deposition charges of light and dark deposited samples was calculated and drawn in Fig. 2. This difference is related to the photogenerated charge in the sample and should give an estimation of V_d which can provide Cu_2O with the highest photoresponse. The highest difference in thickness and deposition charge between dark and light deposited samples reaching values of 1.18 μm and 1.19 C·cm^{-2}, respectively, is observed for $V_d = -500$ mV vs. Ag/AgCl (Fig. 2).

SEM and XRD studies were carried out to inspect the structural properties of samples. Figure 3 shows an XRD plot for structures deposited under light and dark, respectively. The data revealed the presence of 5 dominant diffraction peaks, which are attributed to Cu_2O diffractions (111), (200), (220), (311), (211) (PDF 00-005-0667). Diffraction peaks of Cu or CuO were not observed in the measured data. The diffraction peak indicating Ag belongs to the substrate. The XRD data were used only for identification of layer composition. The identification of the dominant orientation is not provided due to the difference in the layer thicknesses and thus possible errors in the comparison of the intensity ratios.

Figure 4 shows SEM images of structures prepared at dark (a-d) and under light (e-h) at various deposition voltages $V_d = -350$ mV for structures a, e; $V_d = -400$ mV for b, c; $V_d = -500$ mV for c, g; and $V_d = -600$ mV for d, h, all considered vs.

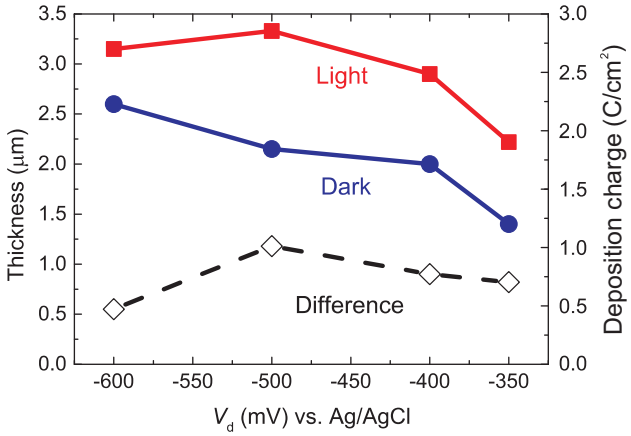

Fig. 2: Thickness of light and dark deposited Cu_2O layers as a function of V_d.

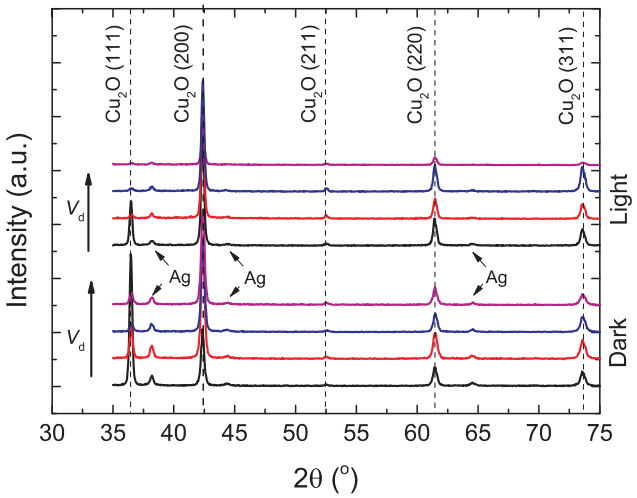

Fig. 3: XRD diffraction measurements of Cu_2O samples deposited a) under dark and b) under light.

Ag/AgCl reference electrode. The truncated triangular pyramid grain shape together with octahedral grains are presented in both types of deposition at low $V_d = -350$ mV vs. Ag/AgCl. Upon the increase of the V_d, the four-sided pyramid grain shape became more dominant. Such grain shape was also observed in the study of Wang et al. [11] for Cu_2O prepared from electrolyte with pH 12.5. A larger grain size is obtained for samples deposited at low cathode $V_d = -350$ mV vs. Ag/AgCl for both types of deposition compared to higher cathode V_d. The increased frequency of nucleation is the source of the grains with a smaller size at higher cathode V_d [12].

Linear sweep voltammetry under the light of solar simulator (1000 W·m^{-2}, AM15) was carried out to investigate the photoresponse of the prepared Cu_2O structures. Figure 5 shows the LSV curve for Cu_2O structure deposited at -500 mV vs. Ag/AgCl under the light. The photoresponse ΔI_{phot} was determined as the difference between the illuminated and dark part of the LSV curve at a voltage close to 0 V vs. RHE. ΔI_{phot} calculated in the same way for all structures is shown as a function of V_d in Fig. 6. The light deposited structures exhibit an increased value of ΔI_{phot} upon the increase of cathode V_d with a maximum of $\Delta I_{phot} = 3.37$ mA·cm^{-2} at $V_{dc} = -500$ mV vs. Ag/AgCl. A further increase of cathode V_d causes a decrease of ΔI_{phot}. All light deposited Cu_2O exhibit higher ΔI_{phot} compared to dark deposited structures. The maximum of the photocurrent observed for the sample deposited at -500 mV vs. Ag/AgCl is in agreement with the above prediction based on the comparison of the thickness between dark and light deposited samples.

Since samples of different thicknesses are compared in this study, it is necessary to clarify the possible impact of thickness on the photoresponse. The diffusion length of the carriers reported in the literature reaches a value of 25–430 nm [5] and [13]. This is a significantly lower value compared to the thickness of the samples. Due to the sufficient thickness of all samples and a short diffusion length, we can expect that the photogenerated carriers are collected only from the top part of the layer. Because of this, the difference of the photoresponse is not due to the difference in the thicknesses between dark and light deposited layers. The Atomic Force Microscopy (AFM) study of samples deposited at $V_d = -500$ mV vs. Ag/AgCl revealed only a small difference in the surface area between light and dark deposited samples. The possible change of the surface area is thus not the source of the photoresponse difference. The detailed AFM study will be provided in the forthcoming publication.

Two main requirements for the high photoresponse of the photovoltaic material are high absorption of the light and high collection of the photogenerated carriers. Due to the low diffusion length, the low collection is the main limiting factor for the photoresponse in the case of Cu_2O. The electrical parameters such as carrier mobility and carrier concentration affect the collection of the photogenerated carriers. It was shown, that such electrical parameters are affected by the deposition conditions and structural morphology of the layer [14] and can be the source of the different photoresponse measured for light and dark deposited samples. In our case, however, the samples prepared on conductive Ag substrates did not offer the possibility to inspect by standard Van der Pauw and Hall measurements. Because of this, such data are not provided on prepared samples in this study. Further experiments are required to inspect the electrical properties and their impact on the photoresponse of Cu_2O samples deposited under light and under dark.

4. Conclusion

Potentiostatic electrodeposition conducted under dark and light at various deposition voltage was used for the preparation of Cu_2O structures. Dark and light deposited structures were characterized by SEM, XRD and by photoelectrochemical measurements. It is shown that the application of illumination during the potentiostatic electrodeposition causes photogeneration of carriers and decreases the resistance of the Cu_2O layer. This allows achieving a higher deposition current and thus a higher growth rate, which results in a higher thickness of the layer. XRD revealed Cu_2O composition of all structures deposition within V_d range used in this study. SEM characterization revealed the lower grain size for higher deposition voltages, which was associated with the higher frequency of nucleation. Light deposited structures exhibit a higher photoresponse compared to structures prepared under dark. The strong relationship of photoresponse with the deposition voltage for structures deposited under light underlines the requirement for adjustment of proper deposition conditions for achieving high photoactive Cu_2O structures for water splitting.

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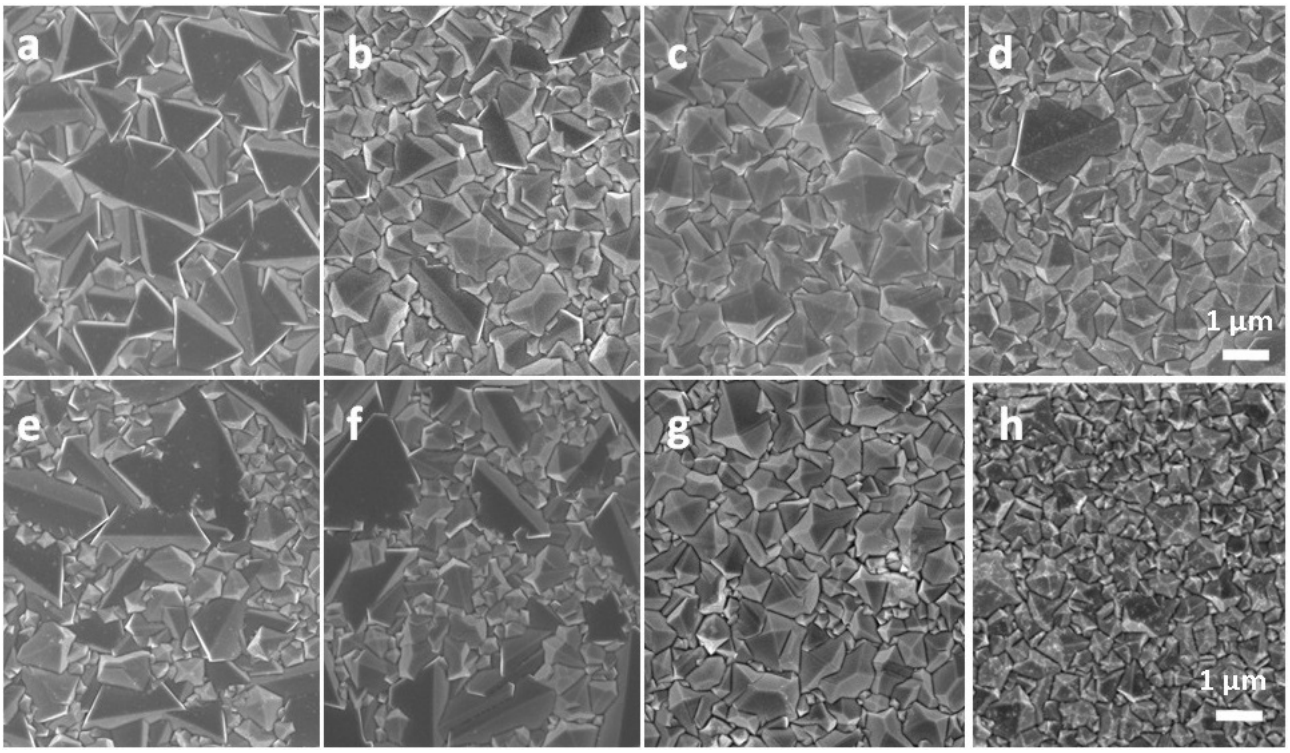

Fig. 4: Cu_2O structures prepared under dark (a–d) and under light (e–h) with deposition voltages $V_d = -350$ mV for structures a, e; $V_d = -400$ mV for b, c; $V_d = -500$ mV for c, g; and $V_d = -600$ mV for structures d, h. All V_d are considered vs. Ag/AgCl reference electrode.

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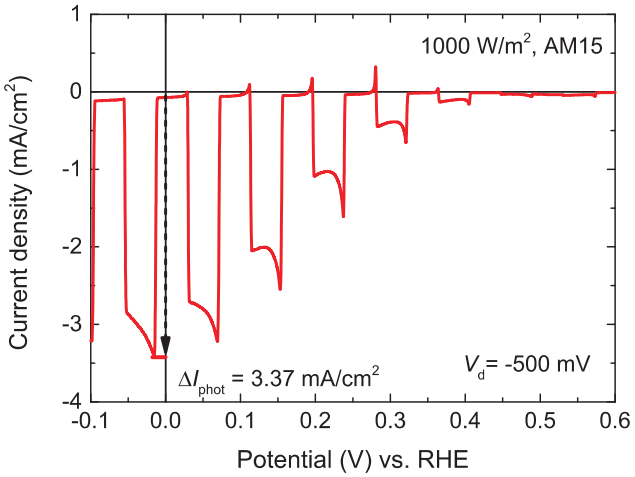

Fig. 5: LSV measured on the best light deposited samples prepared at $V_d = -500$ mV vs. Ag/AgCl.

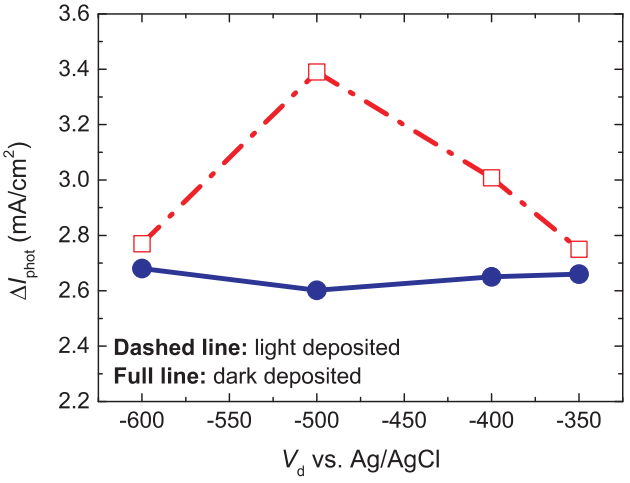

Fig. 6: Photoresponse as a function of V_d vs. Ag/AgCl for light and dark deposited structures.

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