



FABRICATION AND ELECTRICAL CHARACTERIZATION OF Cu-Cu₂O PHOTO ELECTRO CHEMICAL SOLAR CELLS

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ABSTRACT

Solar energy is recognized as a unique conventional energy source. Photoelectrochemical solar cells (PEC) of copper (i) oxide (Cu₂O) is studied in this work on account of its non-toxic nature and the low cost of the material. Copper (i) oxide is prepared by partial thermal oxidation of copper foils at 970°C and used as one electrode, while copper foil is used as the counter electrode. The photo electrochemical solar cells (PEC) device is contained in a cylindrical white plastic container (which is transparent to light) using sodium chloride as an electrolyte. When tested under full sunlight in Katsina town, a short circuit current (I_{sc}) of 180 μA, an open circuit voltage (V_{oc}) of 70 mV, a fill-factor (FF) of 0.27, and an electrical power conversion efficiency, (η) of $1.013 \times 10^{-3}\%$ were obtained respectively.

Keywords: Copper (i) oxide, annealing, photoelectrochemical solar cell, thermal oxidation

INTRODUCTION

Cuprous oxide (Cu₂O) and cupric oxide (CuO) deliver an exceptional opportunity in modifying the band gap into an extreme proficiency for photoelectrochemical and solar cell uses (Abdurrahman *et al.*, 2023). Cu₂O its practically good electrical properties and gains the greatest attention due to its great optical absorption coefficient within the visible range (Musa *et al.*, 1998), non-toxicity, profuse (Wadia *et al.*, 2009), and electrical transformation hypothetical proficiency of 20% for homojunction solar cell (Rakhshani, 1986). Numerous methods comprising thermal oxidation, electrochemical deposition, magnetron sputtering, pulsed laser deposition and chemical vapor deposition has been widely employed to grown the Cu₂O film (Minami *et al.*, 2013; Lee *et al.*, 2014; Musselman *et al.*, 2012; Eisermann *et al.*, 2012; Ruhle *et al.*, 2014) amongst which the thermal oxidation technique typically show reasonably extended smaller carrier transport length and great excellence crystalline, prominent to greater power transformation efficiency (Abdurrahman *et al.*, 2023). Minami *et al* reported a devices with Cu₂O layer manufactured by this technique having the highest efficiency of 6.1%. The band gap energy of a cuprous oxide of about 2.09 eV shows that the material is an intrinsic semiconductor of the P-type (Malerba *et al.*, 2011). It is challenging to attain a great proficiency for Cu₂O solar cell based, because of the incapability to achieve Cu₂O solar cell in the form of N-type for homojunction (Robertson & Clark, 2011; McShane and Choi, 2012).

Cuprous (I) oxide, (Cu₂O) and Cupric (II) oxide, (CuO) are the most considered transition metal oxides because of their exciting characteristics as a P-type semiconductor having a band gap of almost 1.2 and 2.2 eV, correspondingly (Xu *et al.*, 2006; Zhang *et al.*, 2014). In thin film lithium batteries cuprous oxide (Cu₂O) is employ as anode material, also in solar cells and is a good semiconductor material (Musa *et al.*, 1998). The purpose of this research is to fabricate Cu-Cu₂O photo electrochemical solar cells. This can be achieved through producing Cu₂O layer by partial thermal oxidation of Cu, annealing of the Cu₂O layers to produce its resistivity.

Subsequently, the open circuit voltage, the short circuit current of the obtained solar cell are determined. In addition, the current-voltage characteristic of the photo electrochemical solar cell under illumination is measured.

MATERIALS AND METHODS

This section reveals the steps applied in obtaining copper (I) oxide, Cu₂O primarily from the primary element, copper, Cu are revealed. It is important in the synthesis of Cu-Cu₂O photoelectrochemical solar cells, to acquire a P-Cu₂O metal oxide semiconducting material firstly (Abdurrahman *et al.*, 2023).

Cutting and Cleaning of Copper (Cu) Samples

High purity copper of thickness 0.1mm of about 99.97% in the form of foils were incision into normal size wafers of 4cm x 4cm, acid rinsed and then thoroughly washed with distilled water, dried and clean in envelopes ready for high temperature oxidation (Abdurrahman, 2019).

Thermal Oxidation of Copper Samples

The oxidation was conducted in a furnace at high temperature with automatic temperature regulation. The furnace is able to sustain any pre- set temperature to within $\pm 2^\circ\text{C}$. The oxidation temperature was set at 970°C (Abdurrahman *et al.*, 2022). The samples was hold using a ceramic crucible. The samples were arranged at the interior of the furnace immediately the pre-set oxidation temperature was reached. When the oxidation time is attained the oxidation process was stopped (i.e. 5 minutes) by quenching the oxidized samples in purified water and dehydrated with tissue paper then lastly in air (Musa *et al.*, 1998; Abdurrahman, 2019).

Annealing and Quenching

The samples were annealed at temperature of 500°C in order to enhance the performability of Cu₂O (Ohajianya, *et al.*, 2013). Reducing the temperature of the furnace to desired annealing temperature, the annealing was done for 1 hour. After annealing, the samples were removed from the furnace

and immediately slaked in purified water and dried with tissue paper.

Chemical Etching

Once the oxidation and annealing processes were completed, the samples turned black (Abdurrahman *et al.*, 2023). This black coating signified the existence of copper (ii) oxide (CuO). The oxide layer is not needed in this research and hence chemical etching was carried out to remove it. This process was carried out in three stages as follows (Musa and Yunusa, 2013);

- i. 5g of FeCl₃ and 4g of NaCl were immersed in 150ml of purified water at room temperature. 20cm³) of strong

HCl were then inserted gently to the solution. The samples were then dipped in to this solution and gently shaken for about two minutes until the reddish brown colour of Cu₂O appeared. The samples were removed immediately, rinsed quickly in purified water at room temperature and finally desiccated between tissue papers.

- ii. It should be noted that prior to the first etching process i.e. after oxidation and annealing process, the structure of the form was obtained as shown in figure 1 (a) and (b) below:

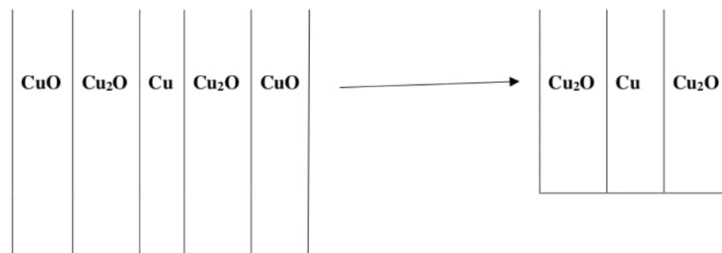


Figure 1: Illustration block for the etching procedure.

Afterward the black CuO layer is stripped off so that we now have the structure as shown above.

- iii. Copper (i) oxide on one side of the above structure was removed using concentrated hydrochloric acid to obtain the final structure used for the photo electrochemical solar cell as shown below:

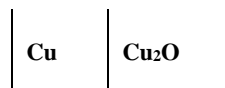


Figure 2: Structure of copper (i) oxide for photochemical solar cell

Fabrication of the Photo Electrochemical Solar Cell

Thirty gram (30g) of sodium chloride (NaCl) was dissolved in 150 mL of distilled water in a cylindrical plastic vessel. Copper wire electrodes were made to the Cu₂O and the pure

Cu surfaces by means of silver paste and sited inside a plastic vessel that is transparent to light (Abdurrahman *et al.*, 2023). A complete circuit was then made to a micro ammeter as shown in the figure 3 below:

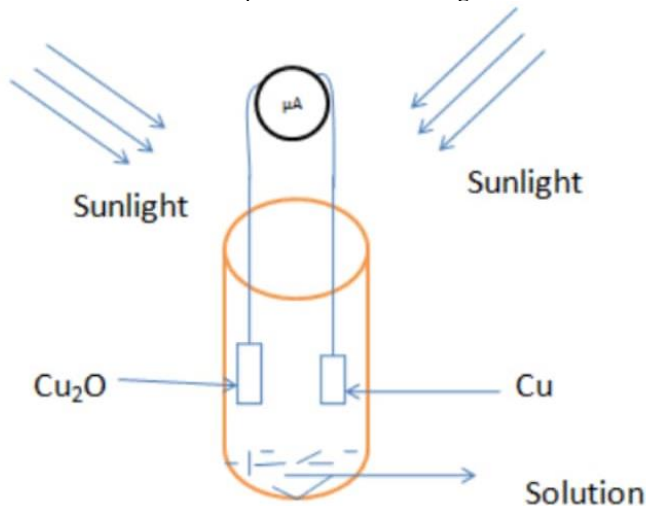


Figure 3: Fabrication of Cu-Cu₂O Photoelectrochemical Solar cell.

RESULTS AND DISCUSSION

The photocurrent and photo voltage achieved under illumination by the fabrication of the sample (Cu-Cu₂O) is presented in table 1 below in which the fabricated Cu-Cu₂O photo electrochemical solar cell displayed characteristic curves with open-circuit voltage and short-circuit current followed by power efficiency conversion. A maximum photocurrent and photo voltage of 180μA and 70mV

respectively was obtained at the same time of the day. While tested in Katsina town of Katsina state, Nigeria, the computed external parameters of the developed sample delivered the short circuit current (*I*_{sc}) and open circuit voltage (*V*_{oc}) of 600μA and 70mV correspondingly with the electrical power conversion efficiency (η) of 1.013 x 10⁻³ % and fill factor (FF) of 0.27. The external parameters measured for the Cu-Cu₂O sample prepared are displayed in table 2 below.

Table 1: The current voltage characteristic value under illumination

I (μA)	V (mV)
350.	35
220	60
180	63
350	50
270	70

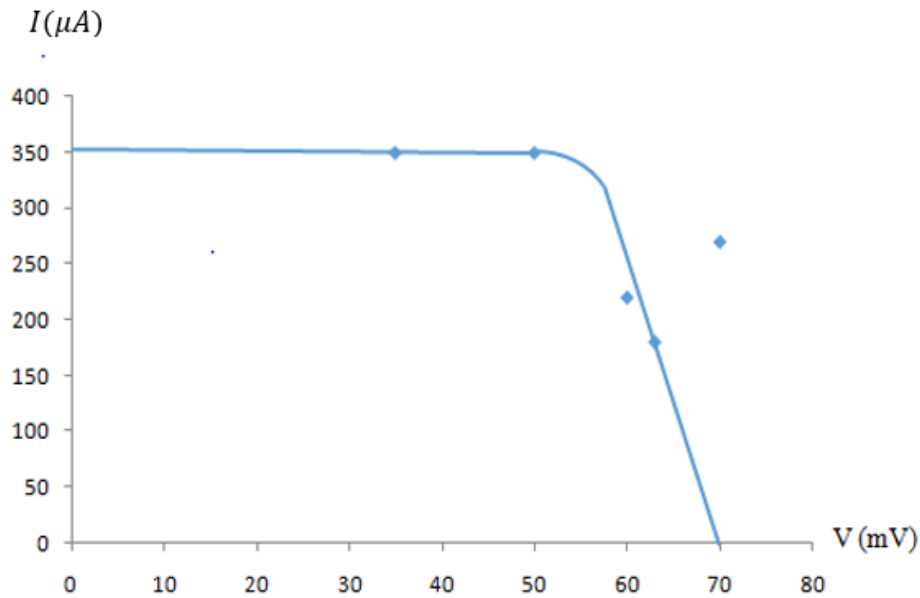


Figure 4: Current – Voltage characteristics of the photochemical solar cell under illumination.

Table 2: The external parameters of the solar cell gain under illumination

V _m (mV)	I _m (μA)	V _{OC} (mv)	I _{SC} (μA)	P _{max} (x10 ⁻⁵ W)	FF	Efficiency (x 10 ⁻³ %)
63	180	70	600	1.134	0.27	1.013

Ohajianya and Abumere, (2013) fabricate Copper-Cuprous Oxide (Cu₂O/Cu) by thermal oxidation method, the authors reported a maximum power point, open circuit voltage, short circuit current, and efficiency of the solar cell as 17.76 μW, 86.0 mV, 518 μA and 0.0178%, correspondingly. Abdu, (2017) used thermal oxidation method and obtained an

efficiency of 0.08 in his work fabrication and study of the electrical properties of Cu - Cu₂O photoelectrochemical solar cell.

The performance of the Cu-Cu₂O PEC solar cell with others electrodes improved by thermal oxidation methods stated in the literature are compared as shown in table 3 below.

Table 3: Comparison with related findings in the literatures.

Structure	Method	Findings	Efficiency	Authors
Hg/Cu ₂ O/Hg	Thermal oxidation	η, V_{OC}, I_{SC}	0.50%	Abdurrahman <i>et al.</i> , (2023)
Cu/Cu ₂ O	Partial thermal oxidation	V_{OC}, I_{SC}, FF	$1.55 \times 10^{-2}\%$	Ohajianya, <i>et al.</i> ,(2013)
Cu/Cu ₂ O	Partial thermal oxidation	V_{OC}, I_{SC}, FF	0.4%	Herion, <i>et al.</i> ,(1979)
P-Cu ₂ O/n-ZnO	Partial thermal oxidation	V_{OC}, I_{SC}, FF	0.11%	Masanobu, <i>et al</i> (2007)
Cu ₂ O	Thermal oxidation	V_{OC}, I_{SC}, FF	0.08%	Abdu (2017)
Cu/Cu ₂ O	Partial thermal oxidation	η, V_{OC}, I_{SC}, FF	$1.013 \times 10^{-3}\%$	Current work
Cu ₂ O	Thermal oxidation	V_{OC}, I_{SC}, FF	0.046%	Abdurrahman (2019)
Cu ₂ O	Electro-deposition	η, V_{OC}, I_{SC}, FF	0.01	Hussain <i>et al.</i> , (2018)

Cu ₂ O	Electro-deposition	η, V_{oc}, I_{sc}, FF	0.28	Hussain et al., (2018)
Cu ₂ O	Electro-deposition	η, V_{oc}, I_{sc}, FF	0.12	Hussain et al., (2018)
Cu ₂ O	Electro-deposition	η, V_{oc}, I_{sc}, FF	0.09	Hussain et al., (2018)
AZO/Cu ₂ O	1-D solar cell capacitance simulator	η, V_{oc}, I_{sc}, FF	0.570	Daniel et al., (2021)
AZO/ZnO/Cu ₂ O	1-D solar cell capacitance simulator	η, V_{oc}, I_{sc}, FF	0.605	Daniel et al., (2021)
Ni/Cu ₂ O/Cu	Electro-deposition	η, V_{oc}, I_{sc}, FF	$0.7 \times 10^{-2}\%$	Georgieva et al., (2011)
SnO ₂ /Cu ₂ O/C	Electro-deposition	η, V_{oc}, I_{sc}, FF	$0.41 \times 10^{-2}\%$	Georgieva et al., (2011)

In comparison to these results, the developed electrode show the performance for photoelectro chemical solar cells applications.

CONCLUSION

In this work by partial thermal oxidation of high purity copper foil at high temperature of 970°C, it has been shown that P-type Cu₂O layers of adequate properties for photo electrochemical solar cell is possible. The future development and use of these cells for commercial use is very promising. A substantial reduction of the series resistance and hence the resistivity of the Cu₂O layer was achieved by annealing. Copper (i) oxide is known to be a semiconductor of P-type, as grown mainly because of its non-stoichiometric nature. The main impurity centers, acceptors in this case, are probably vacant copper lattice sites. Photo currents and photo voltage were successfully detected in the fabricated photo electrochemical solar cell. I_{sc} , V_{oc} , and FF of values 180 μ A, 70 mV and 0.27 were obtained respectively. An electric power conversion efficiency (η) of $1.013 \times 10^{-3} \%$ was calculated from the fabricated photo electrochemical solar cell with a maximum power, P_{max} of 1.134×10^{-5} W

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