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Enhancement of Photoelectrochemical Solar Cell Performance by Surface Modification of Cu_2O using Hg heteroepitaxial growth

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Abstract
Cupric oxide (Cu_2O) thin films have been synthesized on copper (Cu) substrates using thermal oxidation method. The heteroepitaxial growth Hg/Cu_2O/Hg thin films were successfully grown on Cu_2Oprepared with soaring stability and superiority in various compositions by an economic, simple and reliable microwave oven method using Bromine powder as transporting agent. The influence of the substrate and heteroepitaxial growth on the structural properties of copper II oxide films was discussed. The formations of Cu_2O thin films are further identified by Fourier transform infrared spectroscopy. PEC performances of the Hg/Cu_2O electrodes containing different peak structures were determined, and the changes of PEC activities were examined comparatively. The photovoltaic properties demonstrated by the sample have been found to act as photocathodes and they have p-type conductivity. The synthesized PEC solar cells under illumination of Cu-Hg/Cu_2O/Hg and Cu-Cu_2O results in the short circuit current density (I_{SC}) of 50.0 and 0.14mA, power conversion efficiency (PCE) of 0.50and 0.036%, and open-circuit voltage (V_{oc}) of 18 and 11.0mV respectively. Our findings reveal that the PCE of Hg/Cu_2O/Hg heteroepitaxial growth thin-film PEC solar cell is enhanced through the usage of Hg as absorber layer in comparison to the Cu_2O stratum.

Keywords: cuprous oxides; photocathodes; photovoltaic; Cu_2O; heteroepitaxial

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Introduction

Copper oxide (Cu_2O) is a reddish p-type semiconducting material that is fascinating due to its unswerving bandgap of 2.0 to 2.2 eV forming acceptor levels 0.4eV directly above the valence band ensuing from the presence of Cu vacancies (Jongh *et al*., 2011); which turn into an auspicious material for converting photovoltaic energy into chemical and electrical energy (Nian *et al*., 2008; Siripala *et al*., 2003). Cupric oxide Cu_2O is extensively used in photocatalysts and as a photoelectrode for electrochemical cells (Yoon *et al*., 2000). Cu_2O water splitting activeness particularly beneath visible light irradiation for the making of hydrogen fuel has been the center of attention (Hara *et al*., 1998; Hu *et al*., 2008). Cupric oxide is also widely used in gas sensors, antifouling, magnetic storage devices, micro-nanoelectronics, biosensing and catalysis (Jing *et al*., 2007; Luo *et al*., 2009).In addition, copper oxides also have low perniciousness, a high absorption coefficient and low bandgap which are all valuable qualities (Yoon *et al*., 2000).Cupric oxide nanoparticles are also used as photocatalyst in the photocatalytic decomposition of methyl orange (Tang *et al*., 2008;Yang*et al*., 2006). Cuprous oxide for use as a photocatalyst has many attractive advantages (Huang *et al*., 2009): Cu_2O is less toxic, more environmentally affable, cheaper, more copious and readily available (Siripala *et al*., 2003). The Cu_2O bandgap can be affected by numerous factors, including: the particle size can be adjusted, and visible light can be used not only directly as a photocatalyst, but also as a sensitizing semiconducting material for photovoltaic cells (Fernando *et al*.,2001; Siripala *et al*.,2003). Furthermore, in the visible region cupric oxide Cu_2O has a high absorption coefficient (Li *et al*.,2004) and powerfully adsorbs molecular oxygen O_2. This allows you to trap photoelectrons and confine the combination of electrons and holes. A number of methods such as solution pathways and electroforming are used to synthesize different forms of Cu_2O microcrystals and nanocrystals (Tang *et al*., 2008; Yang *et al*., 2006; Li *et al*.,2004; Gana *et al*.,1994).

Large-scale solar-to-hydrogen technologies, photoelectrochemical (PEC) cells that use earth-abundant materials have received increased attention (Walter *et al*.,2010; Luo *et al*.,2014). Furthermore, under PEC process conditions long-term steadiness of these materials is an important issue (Alexander *et al*.,2014; Yan *et al*.,2017). Cuprous and cupric oxides (Cu_2O and CuO) are among the photocathode materials used in PEC water splitting devices, with advantages such as ease of fabrication, relatively low cost and good band gaps. Cupric oxide of (direct) (2.0 eV) band gap has been deliberated to supply a photocurrent of up to 14.7 mA/cm^2 with a photovoltaic cell efficiency of maximum twenty percent (20%) (Zhou & Switzer, 1998;Morales *et al*.,2014). Wong *et al*. and Minami *et al*. have achieved efficiencies of eight percent (8%) and six percent 6% using devices with $Zn_{1-x}Ge_x$-O and $Al_xGa_{1-x}O$ multicomponent oxide thin films with Cu_2O-based heterojunction solar cells, respectively. Having smaller conduction band offsets (arising from a difference in electron affinity between the p-Cu_2O and the n-type semiconducting materials) these multicomponent oxides act as n-type oxide thin-film window layers. Cupric and cuprous oxides have affirmatory and direct band gaps of approximately 2.0-2.6 eV and 1.3-1.6 eV, respectively. This smaller conduction band of cupric oxide offset leads to a superior device with a good efficiency depending on the synthetic methods and morphology of the nanomaterials (Paracchino *et al*.,2014; Radi *et al*.,2010; Septina *et al*.,2017). Some key challenges prohibit the formation of highly efficient and robust photocathodes although copper oxides absorb a vast portion of the solar spectrum, (Zhang *et al*.,2014; Zhang *et al*.,2014). A short diffusion length of the minority charge carrier is one of the main issues in using copper oxides as a photocathode. Depending on the synthesis method this diffusion length ranges from about 20 to 200 nm, but the film usually needs to be at least 1 µm thick to absorb most of the sunlight. Therefore, it is clear that it is significant to

efficiently separate photo-excited electron-hole pairs. Therefore, a layer-by-layer manufacturing and ribbon bending strategy with the appropriate composite material is used to achieve an efficient copper oxide photocathode (Dubale *et al*.,2016; Yang *et al*.,2016; Li*et al*.,2018). Another issue is the photostability of aqueous electrolytes. Photocorrosion of copper oxide can occur because the redox potential of oxidation and reduction is between the water decomposition potential (Zhang Li *et al*.,2013; Jang Li *et al*.,2015). Much research effort has been made to improve charge carrier collection at photocathodes through doping, co-cathodic decoration (Chen Li *et al*., 2018), and nanostructuring. Engineering (Li *et al*., 2019; Liu *et al*., 2018) and light stability remains the major problems with this material. (Dubale *et al*., 2015, Dubale *et al*., 2016, Tilley *et al*.,2014; Lan *et al*.,2018).

In this work, we focus on the synthesis of cubic Cu_2O films and heteroepitaxial deposition of Hg/Cu_2O/Hg thin film, prepared on Cu_2O substrates by thermal oxidation. The roles of thermal oxidation time and during the deposition of Hg were investigated. Thus, the development of highly stable p-type Cu_2O-basedphotoelectrodes with improved photoelectrochemical solar cell performance is the main focus of this work.

METHODOLOGY

We applied a step-by-step method for the transition of the sample from the starting element copper to the cuprous oxide Cu_2O up to heteroepitaxial growth of Hg. In the synthesis of Cu-Cu_2Ophotoelectrochemical solar cells, it is important to obtain the p-Cu_2O metal oxide semiconducting material initially.

The first stage is cutting and cleaning the sample; Foil-like (0.1 mm thick) commercially available pure copper (99.98%) was cut into 2 cm x 2 cm standard size plaques, the samples were pickled with the edge of the bottle to smooth it and then immersed in dilute HNO_3 solution then rinsed thoroughly with distilled water several times then dried for use in order to removed impurities on the surface of the foil.

The second stage is the thermal oxidation; the power of the furnace was turned on and the oxidation temperature was set to 950°C. The furnace took about an hour to reach the oxidation temperature, the samples were placed in a clay crucible, placed in the furnace, oxidized for 8 minutes and immediately quenched with cold distilled water. The oxidized sample was annealed at a temperature of 475°C to restore the surface of the foil after a long oxidation time with cracks on the surface of the foil. The tempered sample was quenched with cold distilled water and air dried.

The third stage is the Chemical etching after the end of oxidation and annealing, a black surface of CuO (copper oxide) is formed next to the red copper oxide (Cu_2O) with a liver red colour. Black copper oxide was removed by chemical etching. 4 grams of $FeCl_2$ and 4 grams of NaCl were dissolved in 100 mL of distilled water. 2ml of concentrated HCl was added to the solution, and then the sample was immersed inside, shaking carefully until the black colour is entirely engraved. The samples were then removed, rinsed with distilled water and dried between tissue papers and finally in air.

Additional chemical engraving was carried out using 4g of potassium persulphate liquefied in 40ml of distilled water. The samples were finally rinsed in distilled water and dried between tissue papers. The etching process was considered completed when the characteristic liver red colour of Cu_2O appeared. The black CuO layer formed during oxidation was

removed when shaking in a solution of $FeCl_3$, HCl and NaCl, leaving behind the red Cu_2O.

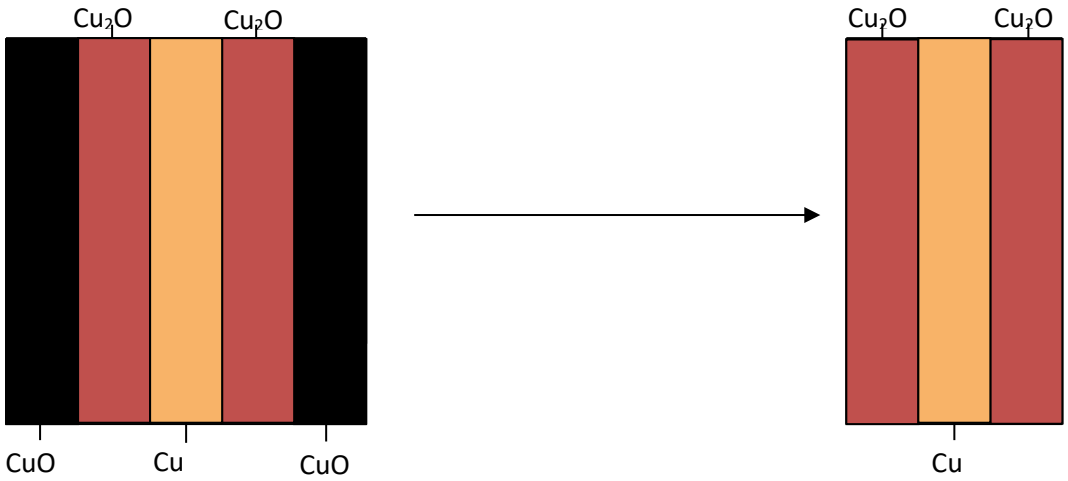

Fig 1.0: The etching procedure Block illustration

Fourth stage is Chemical Vapour Transport,(CVT) (Figure 2.0) which consist of mixing stoichiometric amounts of inorganic compound with the chalcogen. This was carried out using microwave oven for 1 hour in order to study the photo response of the sample at 80°C with the help of the transport agent (Br) in a cylindrical container. The unsealed vacuum was placed in-between the ceramic crucible and then placed in the oven where a microwave radiation creates a magnetic field which continuously alters the surrounding temperature. This leads to the oscillation of the transport agent (Br), forming $Hg/Cu_2O/Hg$ on both side of the sample Cu_2O.

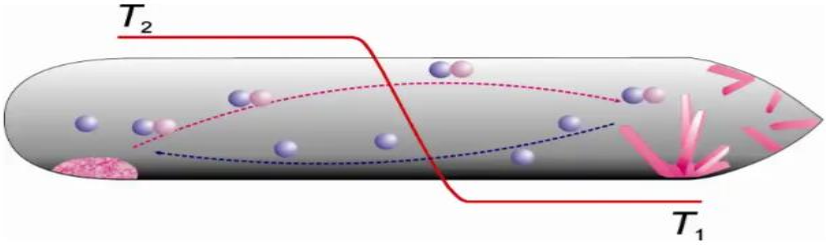

Fig 2.0: compound vapour transportation

The final stage is electric cell manufacture. 1g of Sodium Chloride was decanted into the see-through moldable container. Cu wire electrodes were linked to the manufactured $Hg/Cu_2O/Hg$ and the Cu negative electrode by means of silver paste and both sited within the moldable container. An accomplished electrical route was subsequently completed by linking a micro – ammeter to the two electrodes as shown in fig 3.0.

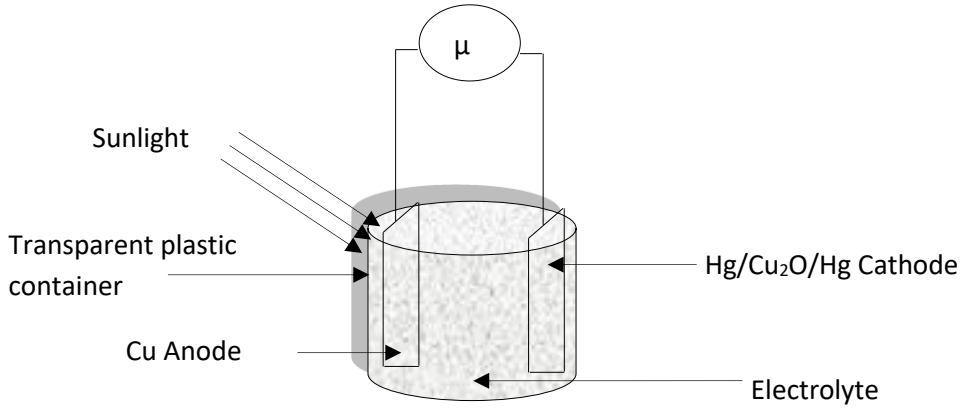

Fig. 3.0: Design of the constructed Hg/Cu_2O/Hg PECs.

RESULTS AND DISCUSSION

The efficiency, maximum power, photo voltage and photocurrent was obtained under illumination as outline in Table 1.0 and the Cu-Hg/Cu_2O/Hg PEC solar cell showed characteristic curves of a number of external parameters followed by transition power efficiency. When analyzing the prototype, the calculated external parameters of the prepared samples Cu-Cu_2O and Cu-Hg/Cu_2O/Hg are stated as shown in table 1.0. Two different readings are recorded using a multimeter and numerous solar irradiances in order to study the solar cell parameters, two dissimilar graphs are studied for two different samples for testing photo response and photo voltage of the electrode under illumination. In table 1.0 it can be seen that for the synthesized Cu-Hg/Cu_2O/Hg, the deposited Hg increases the photo response at the same time increasing the efficiency of the sample. It also works as an absorber layer to generate charge carriers (electrons and holes) under solar light irradiation.

Table 1.0: The photocurrent, maximum power, efficiency and photo voltage of dissimilar reading of Cu-Cu_2O and Cu- Hg/Cu_2O/Hg photoelectrochemical solar cell

S/N	I_{SC}	V_{OC}	P_{MAX}	η
1	0.14mA	11.0mV	1.248×10^{-4}W	0.036%
2	50.0mA	18mV	15.17×10^{-4}W	0.461%

The first row in table 1.0 is forCu-Cu_2O synthesized using thermal oxidation method while the last row is for Hg layer deposited using microwave oven method.

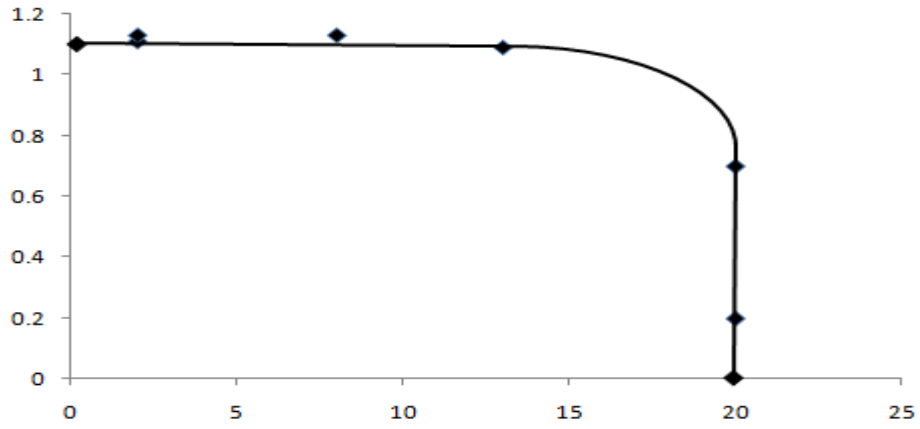

Fig. 4: The graph of Cu-Cu_2O photoelectrochemical solar cell before surface modification

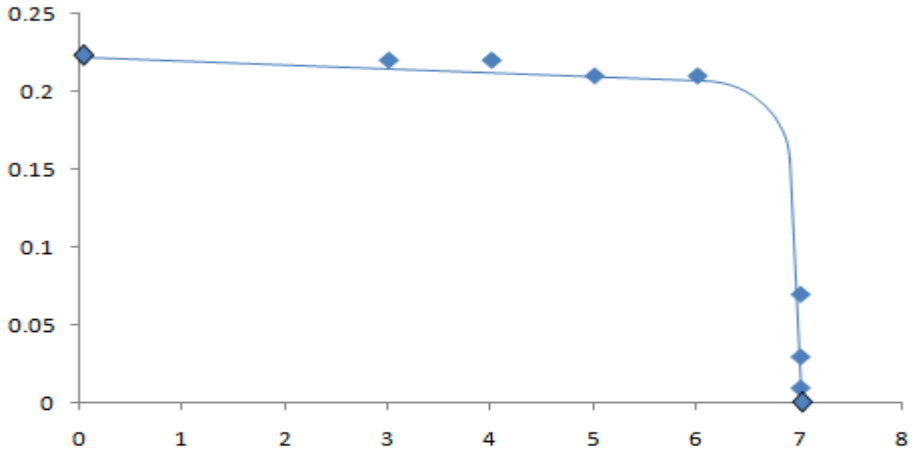

Fig. 5: The graph of Cu- Hg/Cu_2O/Hg photoelectrochemical solar cell after surface modification

By thermal oxidizing technique on cupric oxide substrate at high 950°C temperature of a furnace the photovoltaic properties of Hg/Cu_2O/Hg thin film of the synthesized heteroepitaxial grown sample has shown that cupric oxide thin film can be used as heteroepitaxial grown substrate. We assessed the photovoltaic features of Cu-Hg/Cu_2O/Hg layer in order to examine the performance of the p-type Hg/Cu_2O/Hg thin film as an active stratum. The cupric oxide of thickness 0.4 mm used for the active stratum was fabricated on a copper foil of thickness 0.1mm. Figure 5 shows typical I-V characteristic curve of Cu-Cu_2O thin film. The properties were assessed by exposure to simulated sunlight at air mass of 1.5g. This figure also shows that the synthesized sample act as a photovoltaic cell from the characteristic of the curve.

Figure 6.0 clearly shows the manufactured Hg/Cu_2O/Hg thin film by heteroepitaxial growth as photovoltaic cells with improved solar external properties better than that of synthesized Cu_2O. These results clearly show that the synthesized Hg/Cu_2O deposited on Cu_2O thin film by thermally oxidizing method functions as an active stratum likewise the Cu_2O deposited on

Cu plate. These results suggest that the Hg/Cu_2O thin film with very good crystallinity produced by heteroepitaxial growth is excellent as an active stratum. The work attempted to test the electrical properties of a heteroepitaxial grown Hg/Cu_2O thin film that functions as an active stratum. The electrical properties were evaluated using a conductive substrate Cu_2O to produce the film by thermally oxidizing method. The electrical conductivity of the thermally oxidized Hg/Cu_2O stratum increases the external parameters of the photovoltaic cell (Fig. 6.0). This is due to the fact that the width of the depletion stratum propagating in Hg/Cu_2O decreases with increasing electrical conductivity. The transition efficiency of 0.5% shade more light and possibility that heteroepitaxial growth on p-type thin film deposited by thermally oxidizing method can act as an active layer.

The properties and photoelectrochemical performance of the Cu-Hg/Cu_2O were compared with others modified electrodes reported in the literature. Table 2summarizes the recent works on the thermal oxidation techniques.

Table 2: Comparison of Findings with other Works in Literature

Authors	Structures	Method	Efficiency	findings
Ohajianya, *et al.*,(2013)	Cu_2O/Cu	partial thermal oxidation	0.62×10^{-2}%	*FF, Isc,Voc*
Ohajianya, *et al.*,(2013)	Cu_2O/Cu	partial thermal oxidation	1.55×10^{-2}%	*FF, Isc,Voc*
Herion, *et al.*,(1979)	Cu/Cu_2O	partial thermal oxidation	0.4%	V_{oc}
Masanobu, *et al(2007)*	*p*-Cu_2O/*n*-ZnO	partial thermal oxidation	0.11%	*FF, Isc,Voc*
Ohajianya, *et al.*,(2013)	Cu/Cu_2O	partial thermal oxidation	1.55×10^{-2}%	*FF, Isc,Voc*
Abdu *(2017)*	Cu_2O	Thermal oxidation	0.08%	*FF, Isc,Voc*
Abdurrahman *,(2019)*	Cu_2O	Thermal oxidation	0.046%	*FF, Isc,Voc*
Present Work	Hg/Cu_2O/Hg	Thermal oxidation	0.50%	*η, Isc,Vo*
Jiantuo *et al.,(2020)*	Cu_2O/ $Zn_{0.8}Mg_{0.2}O$ and ECD	Thermal oxidation and ECD	0.55%	*η ,FF, Isc,Voc*
Jiantuo *et al.,(2020)*	Cu_2O/ $Zn_{0.8}Mg_{0.2}O$	Thermal oxidation and ECD	0.99%	*η ,FF, Isc,Voc*
Daniel *et al.,(2021)*	AZO/Cu_2O	1-D solar cell capacitance simulator	0.570	*η ,FF, Isc,Voc*
Daniel *et al.,(2021)*	AZO/ZnO/Cu_2O	1-D solar cell capacitance simulator	0.605	*η ,FF, Isc,Voc*
S.S. Jeong et al., (2008)	ZnO/Cu_2O	Electro-deposition	0.41	*η ,FF, Isc,Voc*
S.S. Jeong et al., (2008)	ZnO/Cu_2O	Electro-deposition	0.276	*η ,FF, Isc,Voc*
Georgieva *et al., (2011)*	ITO/Cu_2O/C	Electro-deposition	2.34×10^{-2}%	*η ,FF, Isc,Voc*
Georgieva *et al., (2011)*	Ni/Cu_2O/Cu	Electro-deposition	0.70×10^{-2}%	*η ,FF, Isc,Voc*
Georgieva *et al., (2011)*	SnO_2/Cu_2O/C	Electro-deposition	0.41×10^{-2}%	*η ,FF, Isc,Voc*
Hussain *et al., (2018)*	Cu_2O	Electro-deposition	0.01	*η ,FF, Isc,Voc*
Hussain *et al., (2018)*	Cu_2O	Electro-deposition	0.09	*η ,FF, Isc,Voc*
Hussain *et al., (2018)*	Cu_2O	Electro-deposition	0.28	*η ,FF, Isc,Voc*
Hussain *et al., (2018)*	Cu_2O	Electro-deposition	0.12	*η ,FF, Isc,Voc*

Based on these results, it could be confirmed that the developed electrode presents the advantage of a heteroepitaxial growth preparation and a high performance for PEC solar cells.

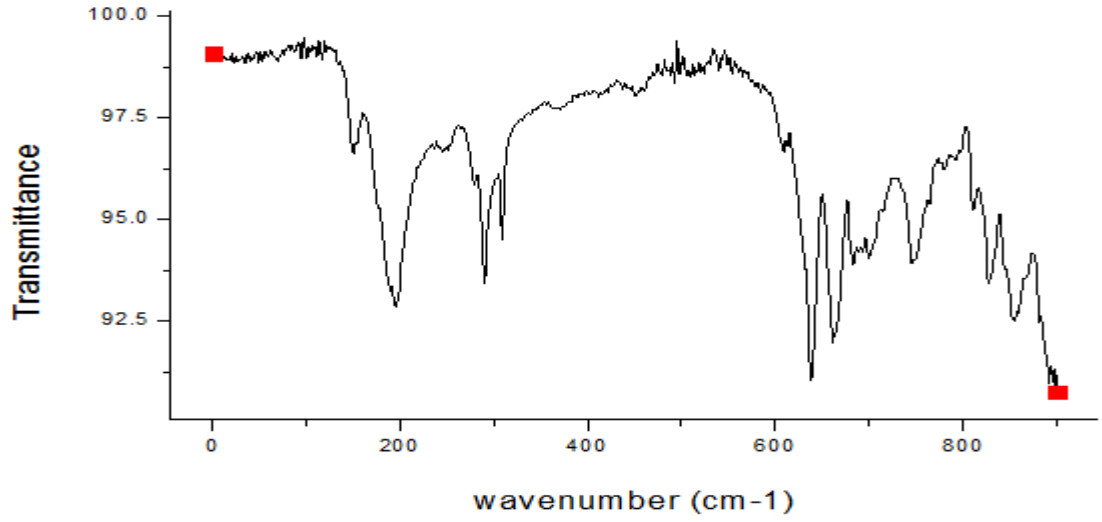

Fig 6: The graphical record of Fourier transform invisible or infrared (FTIR) spectroscopy of analyzed Hg/Cu_2O/Hg in microwave oven for 1 hour

Figure 6.0 shows the analysis of Hg/Cu_2O/Hg FTIR. Based on the number of peaks, there are more than five peaks, indicating that the analyzed chemical is a complex molecule due to the presence of numerous peaks more than five. The peaks of single bond region are perceived at range of (2500-4000 cm^{-1}). Hydrogen bonds are found in a wide absorption band ranging from 3650 and 3250 cm^{-1}(Nandiyanto *et al.*,2019). While for hydroxyl compound it also has been confirmed due to the presence of spectra at frequencies of 1600–1300, 1200–1000 and 800–600 cm^{-1}. The existence of oxygen-related bonding was present due to the presence of sharp bond at about 3506 cm^{-1}. Aromatic structures can be seen with a peak at 3088 cm^{-1} which is in between 3000 and 3200 cm^{-1}(Nandiyanto *et al.*,2019). Narrow bond peaks present at less than3000 cm^{-1} on account to C-C bond. No specific peak of aldehyde was found between 2700 and 2800 cm^{-1}. A range of triple bonds (2000-2500 cm^{-1}) has been observed, indicating the presence of C≡C bonds in the material (Nandiyanto *et al.*,2018; Nandiyanto *et al.*,2019). For the double bond region (1500-2000 cm^{-1}), a large, sharp peak was observed indicating the presence of a double bond. This indicates that there is a carbonyl double bond of ketone, aldehyde, ester, or carboxyl. A peak of about 1629 cm^{-1} indicates the presence of C = C bonds in the sample. The peak of 1462 cm^{-1} represents an aromatic ring. The 3275 cm^{-1} band represents the -NH stretch.1629 cm^{-1} is assigned to symmetric C-H stretch vibration. 1542 $cm^{-1}$is a peak represents N-H bending vibration.1439 $cm^{-1}$is due to C-H bending vibration.

Based on above interpretation, some conclusions can be drawn. The material analyzed has a hydrate component. This sample contains components related to ketones and the material has triple bonds. The material should be a small organic compound, as there are only about 10 peaks. The absorbance visible below 1500 cm^{-1} is the frequency of fingerprints, which are very characteristic of the whole molecule; they tell us what's happening around the molecule, even that part of the infrared spectrum, but some functional groups absorb it. Compounds that correlate with vinyl were also detected at about 800 cm^{-1}. A strong signal was found indicating that aromatic rings are also present. There is a broad and strong peak located at 619 cm^{1}which is very close to 615 $cm^{1}$and that belongs to Cu_2O (Balamurugan & Mehta 2001). A combined band of –CH_2, –OCH and – CCH bending vibrations is observed at 1462 cm^{1}followed by a strain band of –OCH, –COH and – CCH at 1388 cm^{1} (Ibrahim*et al.*,2006).

Conclusion

The present investigation demonstrates an easier, simple and novel method for the preparation of stable absorber stratum on cupric oxide substrate at room temperature. Cupric oxides that were prepared with the thermal oxidation method at950°Cweresubsequently annealed at a temperature of 475°C, and the formed structures and peaks were examined.PEC performance of the copper oxide electrodes containing a different phase structure were determined, and the changes of PEC activities were examined comparatively. The PEC studies reveal photocathode characteristic and the p-type nature of cupric oxides. Thus, the Hg/Cu_2O/Hg semiconductor prepared at 80°C-100°Cinside a microwave oven with aid of molecule spins crossways the unsealed tubing rendered an energetic strength planned for the deposition of Hg with the assistance of the conveying agent (Br) shows the best PEC performance when compared with Cu-Cu_2O.Thus, by using the microwave oven method, Hg/Cu_2O/Hg heteroepitaxial growth of Hg were successfully prepared. The crystal dimensions expand as the cube-shaped Cu_2O transforms into CuO, crystal surface areas increase, crystal shapes change and turn gradually into Hg/Cu_2O.Finally, there is a broad and strong peak located at 619 cm^1in the absorption spectrum, which shows the presence of Cu_2O with higher absorption performance in visible light range. The power conversion efficiency (PCE)of the Hg/Cu_2O samples was about 0.50% with highreproducible.

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