ExploringCuBiSe/Y_2O_3Nanocomposite Material as a Working Electrode In Photoelectrochemical Cell

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ABSTRACT

CuBiSe/Y_2O_3nanocompositeswere synthesized using hydrothermal process. The phase formation and crystallite structure were confirmed by XRD. Morphology structure and the elemental composition were revealed through SEM and EDAX.The optical study shows that the CuBiSe/Y_2O_3 nanocompositehas absorptioncoefficient (0.95 – 1.68cm^{-1}) and theband gap value estimated as 1.72eV.FTIR spectrum reveals all vibrational modes existingin CuBiSe/Y_2O_3. The excitation of electrons for the prepared sample was detected by FL studies. Cyclic Voltammetry graph shows better reduction process and increasing photocurrent. From J-V curve, the open circuit voltage (V_{oc}=.123V), short circuit current (J_{sc}=1.6mA),Fill factor (FF=.356) and efficiency as 0.07 %.

Keywords: Copper bismuth selenide,Yttrium Oxide, Solvothermal Method, Nanocomposite, photoelectrochemical cell

1.1 INTRODUCTION

In the field of nanoscience materials have had the attention, imagination and close scrutiny of scientists in recent year. The results from nano size range make it possible to design and create new materials with improvements in physical properties. As the constituents of nanocomposite have different structures and compositions and hence properties, they serve various functions. In general the nanocomposite materials can demonstrate different mechanic, electric, optical, electro chemical, catalytic and structural properties than those of each individual component [1].

Over the past few years metal selenides have received considerable attention owing to their unusual structures, optical and electronic properties. Metal selenide compounds with nature of semiconductor, have been applied in many areas, such as Photovoltaic cells, solarcells and

LED.In order to make the bandgap match with the solar energy spectrum, researchers added some other metal compound to the promising metal selenides [2].There has been a growing interest in the synthesis of copper selenide, bismuth selenide material due to theirpotential applications in optoelectronic devices, electromechanical devices and thermo electrical devices [3].Yttrium oxide (Y_2O_3) nanoparticle is one of the most important rare earth oxides widely employed in many applications owing to thermal stability, chemical stability and low volatility that leads to adopt high temperature applications.[6]. Most of the yttria based material depends on the crystalline structure and defects present inside materials. Yttria nanoparticles also find useful luminescence applications.[7].

Jiyu et al. (2013) prepared CuBiSe thinfilms by electro deposition method and studied their photo response behaviour using a photo electrochemical cell. Bari et al.(2010) reported the non-stochiometric form of copper bismuth selenide (CBS) films and studied their thermoelectric properties [4].Abirami et al. (2016) prepared CBS thinfilm using vacuum evaporation deposition and studied the photosensitivity of the film [2].Eraky et al.used solvothermal method to synthesise Cu/Bi and Cu/Sb selenide alloys as photoactive electrodes[5].Yttrium oxide (Y_2O_3)nanoparticle is one of the most important rare earth oxides widely employed in many applications owing to thermal stability, chemical stability and low volatility that leads to adopt high temperature applications [6].

However, the previous reports has shown the optical and electrochemical behaviours of CBS thinfilms, none of these studied the behaviour of copper bismuth selenide / metal oxide nano composite. Hence the aim of our present work is to synthesize and study the photochemical behaviour of copper bismuth selenide / metal oxide nanocomposite material. In this paper, the synthesis of CuBiSe nanoparticle done by solvothermal method, $Y_2O_3$is prepared by sonicator method and Copper Bismuth Selenide / Y_2O_3 nano composite synthesized by hydrothermal process and their various characterization studies and electrochemical properties were reported.

2.1 EXPERIMENTAL

2.1.1 Materials

For preparing CuBiSe nanoparticles,Eraky et.al used $Cu(NO_3)_2.3H_2O$, $Bi(NO_3)_3.5H_2O$ and seleniumoxide [5], butin our work we have tried and used Copper oxide, bismuth oxide, selenium powder polyvinylpyrrolidone(PVP), ethylenediaminetetraacetic acid (EDTA), Ethylene glycol, as precursors. Yttrium nitrate and sodium hydroxide are also used.All materials are purchased from Hi media AR grade and are used further without purification.

2.1.2 Preparation of copper bismuth selenide nanoparticles.

Copper bismuth selenide nanoparticles were prepared by solvothermal method. 1g of PVP,1g of EDTA, 0.25M of Copper oxide, 0.5M ofbismuth oxide and 0.13M of selenium powder were added into 80ml of ethylene glycol. The grey coloured solution turned into black mixture under vigorous stirring for 3 hours. The mixed solution was then transferred to Teflon lined stainless steel autoclave (100ml) and heated upto 300˚C in a hotairoven for 5-8 hours. The obtained greenish black products are cleaned by centrifugation at 1600 rpm for 10 minutes, 3 times. The dried nanopartricles were annealed at 100°C for 30 minutes.

2.1.3 Preparation of yttrium oxide nanoparticles.

Using sonochemical method, yttrium oxide nanoparticles were prepared. 0.5 M of yttrium nitrate was dissolved in 10 ml of distilled water and kept under sonication for 90minutes. Meanwhile in another beaker, 0.3M of sodiumhydroxide was dispersed in 30ml of distilled water and allowed to stir for few minutes. The mixed NaOH solution was added drop by drop to yttrium nitrate solution until the pH value reaches 13. The solution was continued to stir at 60ºC for 6 hours[6].The white solution turns into silky white precipitate. The white precipitate is cleaned by centrifugation at 1600 rpm for 10 minutes, 5 times. The purified Y_2O_3 nanoparticles were calcinated at 400ºC in muffle furnace for 4 hours.

2.1.4 Preparation of CuBiSe / Y_2O_3nanocomposite.

CuBiSe / Y_2O_3nanocomposites were synthesized by hydrothermal method by taking 2:1 molar ratio of synthesized CuBiSe and Y_2O_3nanoparticles in 50ml of distilled water and stirred for 60 minutes. The obtained grey coloured solution is transferred into Teflon lined stainless steel autoclave and kept at 300ºC for 2hours in hot air oven. The final synthesized nanocomposites were washed with ethanol and distilled water few times,allowed to dry under room temperature and then annealed at 100ºC for 30 minutes.

3.1 RESULTS & DISCUSSION

Fig1.a shows the diffraction pattern of Y_2O_3,where two major peaks are observed at 29.01˚and 30.2˚ corresponds to (111) and (200) plane. Also peaks are obtained at 50.7˚, 59˚ corresponds to (200,220) plane respectively. This reveals that the synthesised nanocomposites are ofcubic, face centredstructure of Y_2O_3which matches with JCPDS card no 43-0661 and confirms the crystalline formation of nanoparticles. The average crystallite size of Y_2O_3nanoparticles was calculated using Debye-Scherrer's formula, D is found to be 17.23 nm which is better size

compared to previous reports.Fig1.b shows the diffraction pattern of CuBiSe nanoparticles. The prominent peaks are observed at 28.3˚,46˚,56˚,36˚ at (121),(124),(214),(015) planes correspond to anorthic structure and mostly matches with JCPDS card no 80-1592 which confirms the presence of CuBiSe. Also three major peaks are shifted and attained secondary phases at 27˚,44.8˚,50˚ corresponds to (060),(002),(221) planes of Cu_5Se_4 (JCPDS cardno 21-1016). It may be due to lack of correct measurements in stochiometric ratio of materials. However, compare to the earlier reports, our present work shows better results of CuBiSe using CuO,BiO as precursors. Similarly the diffraction peaks of CuBiSe / Y_2O_3nanocomposites are shown in fig 1.c. The major peaks are observed at 28.3˚,36˚,46˚,corresponding to(111),(200),(220) planes confirm the formation of yttriumoxide present in the composite material ,also matches with JCPDS card no 43-0661. The observed pattern of all other prominent peaks of 30.2˚, 44.5˚, 27.9˚, 32.5˚, 46.1˚at (114), (115),(113), (212) planes matches with JCPDS card no 80-1592 which confirms the presence of CuBiSe in the composite material. The crystallite size for the maximum intensity peak at 27.90˚ is 10.95nm and the average crystallite size of CuBiSe / Y_2O_3nanocomposite is found to be 203.5nm.

The surface morphology of annealed nanocomposites was investigated by scanning electron microscopy. Fig 2.1revealsthe surface morphology of CuBiSe / Y_2O_3composites have small flattened hexagon shaped particles are stacked together. These small hexagon flakes geometrically grew with bigger hexagonal orientation reaching about 90 to 120 nm. SimilarlyFig2.2shows the EDS spectrum of CuBiSe / Y_2O_3nanocomposite. It shows the elemental analysis of atoms present in the CuBiSe / $Y_2O_3$with 72 atom % of Cu which may be due to the phase transition of Cu_5Se_4 in CuBiSe nanoparticles. It also confirms the efficient crystallization for CuBiSe / Y_2O_3compounds without impurities. Likewise, Fig2.1d reveals the surface morphology of CuBiSe nanoparticles have flake like shape which agrees with previous reports. [5].

The optical absorbance for bothCuBiSe andCuBiSe /Y_2O_3 samples in UV range was observed. The absorbance coefficient α was calculated using Beer's-lamberts law,

$$\alpha = 2.303\ A\ /d$$

where d is the thickness of the film, A is absorbance [14].The maximum absorption coefficient is found to be in the range from 0.95 to 1.68 /cm for CuBiSe / Y_2O_3 sample is shown in fig 3 a. The optical bandgap of the sample is calculated by Tauc and Menth law.

$$\alpha h\nu = A(h\nu - E_g)^n$$

Where hν is photon energy and E_g is the bandgap energy. For direct transition bandgap n= ½ and for indirect transition bandgap n=2. The bandgap of CuBiSe / Y_2O_3 was observed using the graph hν Vs$(\alpha h\nu)^{1/2}$. By extrapolating the linear range of $(\alpha h\nu)^2$ values to hν axis, the observed bandgap of CuBiSe / Y_2O_3 is 1.72eV(fig 3.b). Thus the theortical value of bandgap is calculated as 1.75 - 1.94eV which agrees with the tauc's plot [4, 5].

Fluorescence emission spectra of CuBiSe/Y_2O_3(fig4)was investigated upon excitationwavelength range from 764nm to 788nm. From this spectra the excitation of electrons due to light source are detected. The prepared CuBiSe / Y_2O_3 nanocomposite shows good behaviour in excitation and suggested as desirable material for photovoltaic devices.

FTIR spectra of CuBiSe / Y_2O_3 and CuBiSe nanomaterials are investigated in the wavenumber range from 4000cm^{-1} to 400 cm^{-1}.Fig 5 showsthe spectra of CuBiSe / Y_2O_3 nanocomposite. The strong bond observed at 1383nm is attributed to stretching and bending vibrations of O-H and at3453.92 cm^{-1} is due to theO-H streching vibration mode. Thestretching vibration peak of Y-O bonding appears at 433cm^{-1} and 739 cm^{-1} [10, 11]. The bending vibration for Cu-Se appears at 536cm^{-1},861cm^{-1} and 1113$cm^{-1.}$

3.1.1 Photoelectrochemical(PEC)characterization.

For the photoelectrochemical experiments,a standard three electrode system were carried out. 1g of prepared nanocomposite material was coated on a FTO glass substrate (1cmx1.1cm) using PVA as a binding agent. The coated CuBiSe/Y_2O_3 substrate was annealed at 60ºC in a hotairoven and used as a working electrode. 0.1 M of sulphuric acid was taken as electrolyte and Ag/AgCl was used as a reference electrode, where platinum wire as a reference electrode. To test the photovoltaic performance, the cell i.e the working electrode was exposed to a light of 500W tungsten filament lamp (intensity 35 mW/cm^2).Fig 6.a shows the CV graph of CuBiSe/Y_2O_3& CuBiSe samples.From the graph, two small cathodic peaks are observed at 0.48V and -1.4V for the CuBiSe/Y_2O_3sample. For CuBiSe , the cathodic peaks are at 0.45V & -1.15 V which is low compare to CuBiSe/Y_2O_3.Likewise, there is a anodic positive shift appears at 0.035V with 0.024 Afor CuBiSe/Y_2O_3 and peaks at 0.01V with 0.01 A for CuBiSe.It reveals that CuBiSe/Y_2O_3 nanocomposite induces the reduction compare to CuBiSe nanoparticle and it corresponds to reactions involving of Y_2O_3[2].

JV curves for CuBiSe/Y_2O_3 is shown in fig6.b .On illumination, the JV curves ofCuBiSe/Y_2O_3 shows a current shift in IV quadrant, indicates the transfer of photoinduced charges which generates the photocurrent [13]. The performances of prepared CuBiSe/Y_2O_3 photoelectro chemical cell's open circuit voltage (V_{oc}), short circuit current density (J_{sc}), fill factor (FF) & efficiency (η)can be calculated using the formula

$FF = V_{max} J_{max} / V_{oc} J_{sc}$

$\eta = FF\ V_{oc} J_{sc} / P_{in}$.

Where P_{in} is the power of the intensity of sunlight [13].

The calculated values are given in the table 1.

4.1 CONCLUSION

Synthesise of CuBiSe/Y_2O_3 nanocomposites using solvothermal method yields a promising results on all characterization studies. The XRD analysis gives the confirmation of presence and formation of CuBiSe/Y_2O_3. The average crystallite size of synthesised sample is 203.5nm, it also agrees with the SEM morphology studies which reveal the CuBiSe/Y_2O_3 nanocomposites have flattened hexagonal particles. The optical behaviour shows the material has better transfering capacity and The maximum optical absorption coefficient is $9x10^5$ and the energy bandgap of the sample is found to be 1.72 eV by using Taucs plot. The PEC parameters have low values may be due to lack of uniformity and stability of conducting substrate. Although, the materials need further optimization in the PEC setup, the advantage with the E_g,lowcost, new set of precursors [9] suggests that CuBiSe/Y_2O_3 nanocomposite via solvothermal/hydrothermal methods is a good choice of exploring the research ideas in photovoltaic and optoelectronicdevices.

Acknowledgement

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Figures and Table

Fig 1: XRD pattern of prepared Y_2O_3, CuBiSe nanoparticles and CuBiSe / Y_2O_3 nanocomposite.

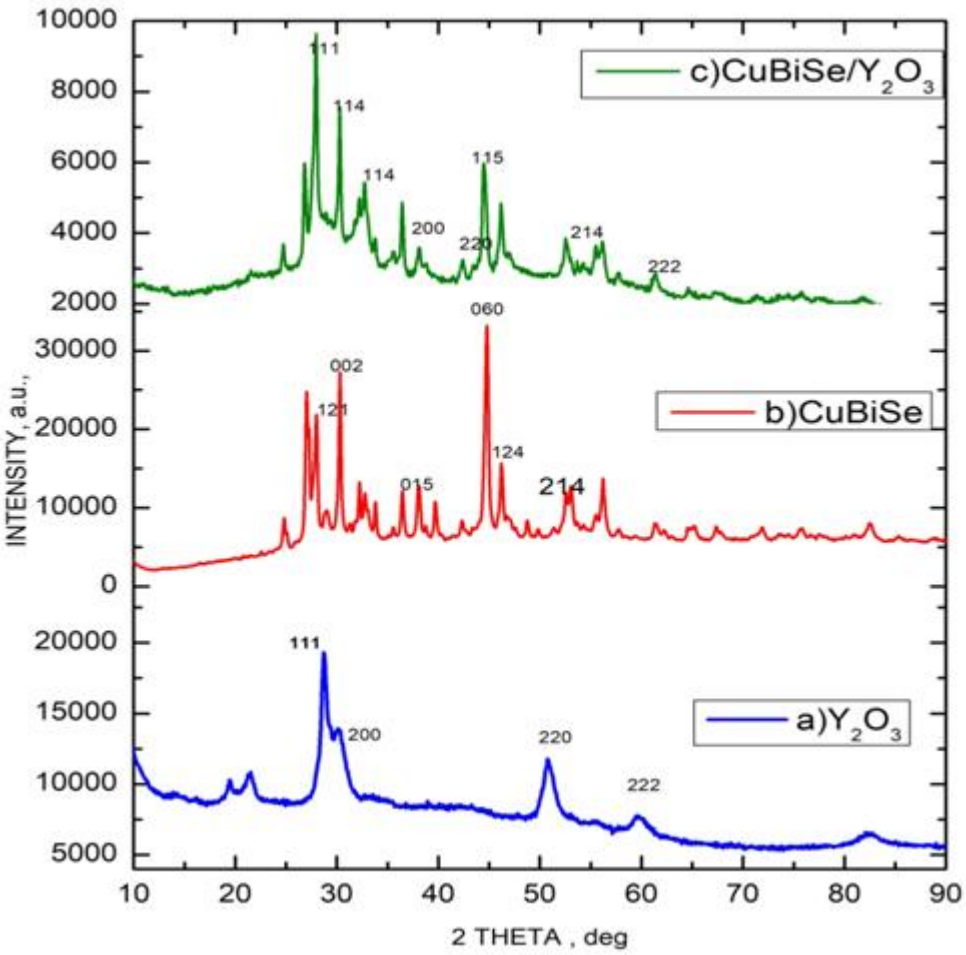
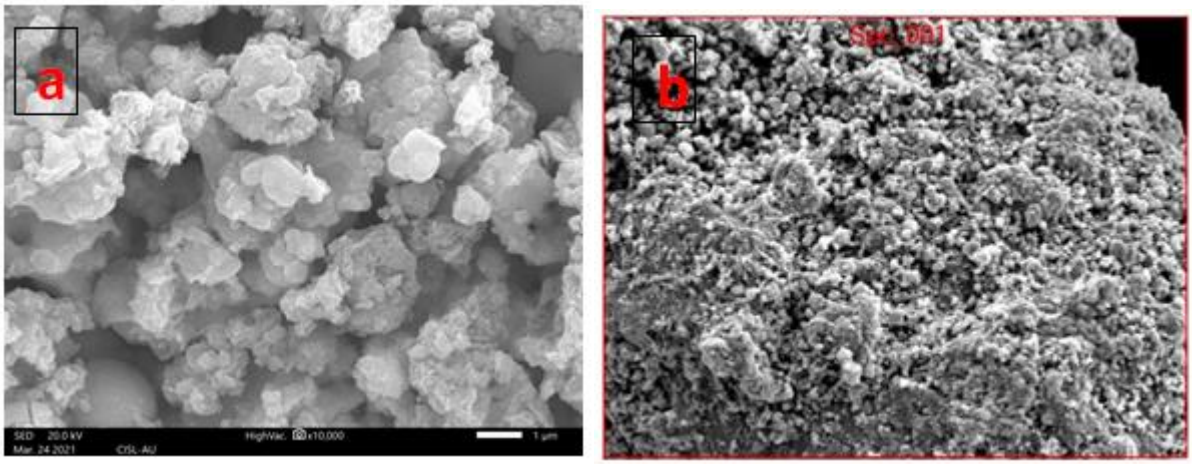


Fig 2(a,b,c) SEM images of CuBiSe / Y_2O_3 nanocomposite at 1µm, 10µm, 500nm.



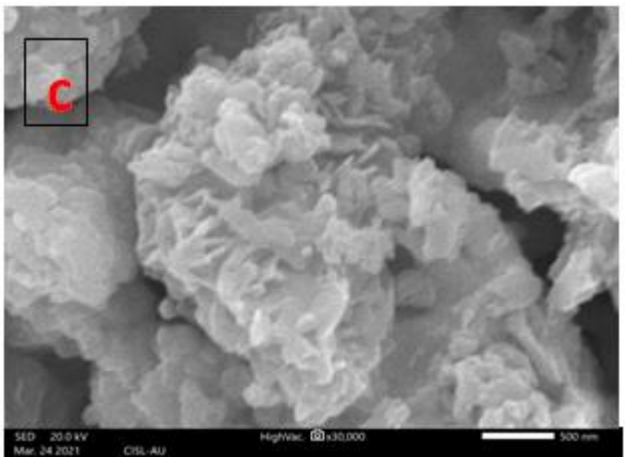


Fig 2(d) SEM images of CuBiSenanoparcticle at 1µm.

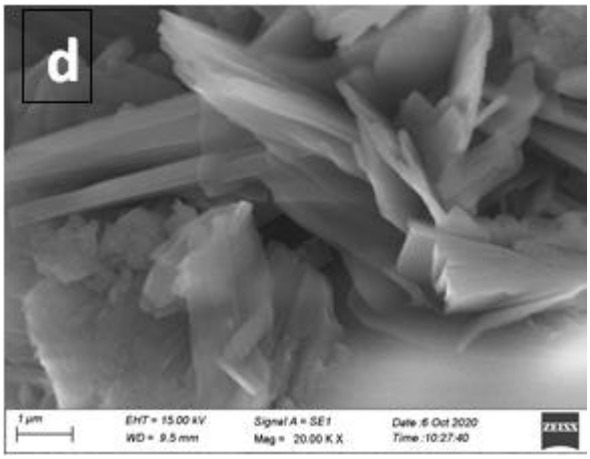
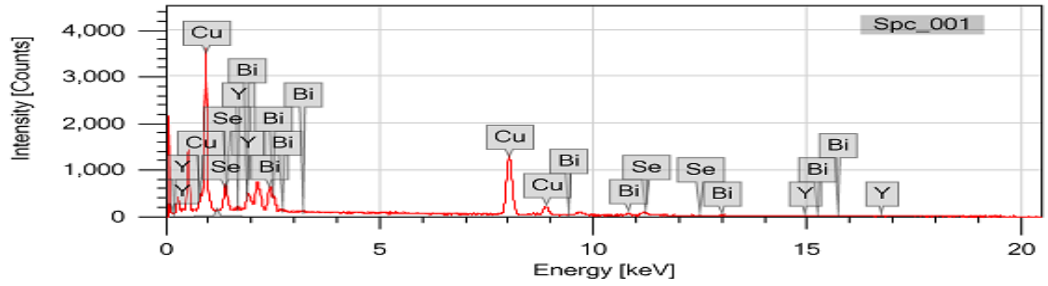


Fig 2.2 EDS Spectrum of CuBiSe / Y_2O_3 nanocomposite



Element	Line	Mass%	Atom%
Cu	K	57.52±0.55	72.37±0.70
Se	L	10.93±0.28	11.07±0.28
Y	L	8.69±0.27	7.81±0.24
Bi	M	22.86±0.38	8.74±0.14
Total		100.00	100.00
Spc_001			Fitting ratio 0.3987

Fig 3(a,b): Tauc's plot and Absorption spectrum of CuBiSe / Y_2O_3 nanocomposite

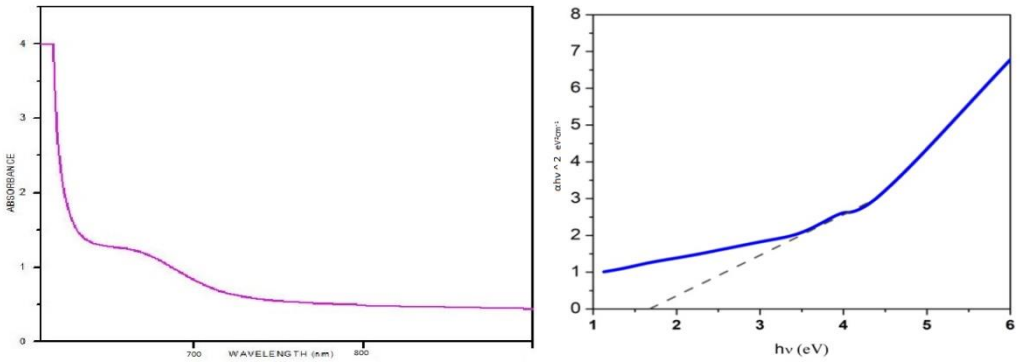


Fig 4: Fluorescence emission spectrum of CuBiSe / Y_2O_3 nanocomposite

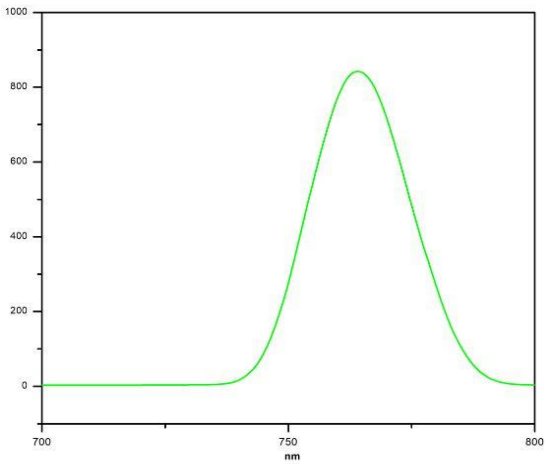


Fig 5 FTIR analysis of CuBiSe / Y_2O_3 nanocomposite

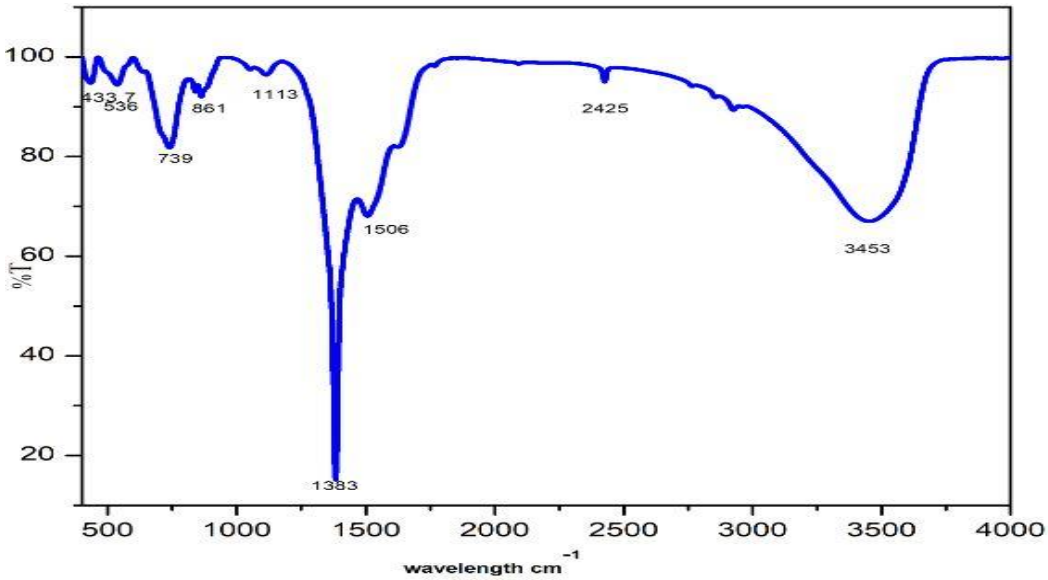


Fig 6.(a): Cyclic voltammetry graph of CuBiSe / Y_2O_3 nanocomposite

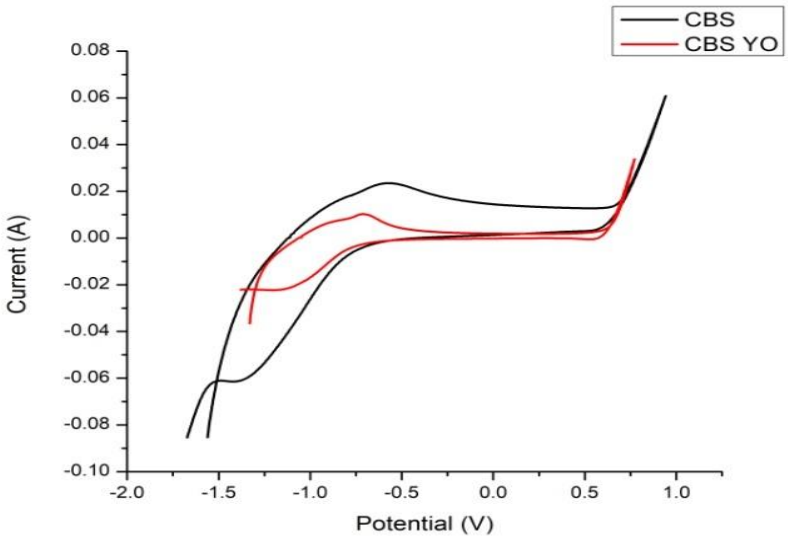


Fig 6.(b): J-V curves for CuBiSe / Y_2O_3 nanocomposite

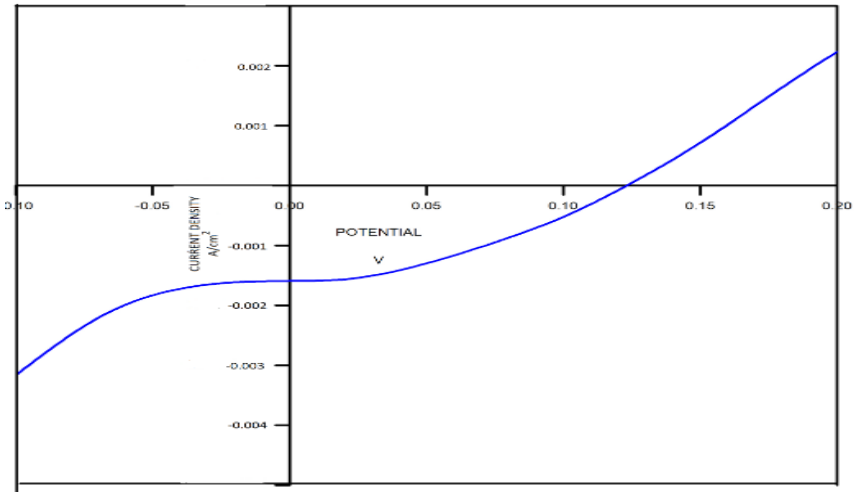


Table 1

Name	V_{oc} (V)	J_{sc} (mA/cm^2)	FF	η (%)
$CuBiSe/Y_2O_3$	0.123	1.6	0.35	0.07

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