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Electrodeposition of n-CdSe/p-Cu$_2$Se Heterojunction Solar Cells

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Abstract

Thin film heterojunction photovoltaic (PV) solar cells play a vital role due to its large area, low cost and higher efficiency devices in solar energy conversion. In this work, low-temperature and cost-effective electrodeposition of n-CdSe and p-Cu$_2$Se heterojunction solar cells are developed and explored. The individual part of heterojunction is screened for its structure, morphology, compositional, optical, and photoelectrochemical measurements. Then-CdSe/p-Cu$_2$Se device designed onto an indium-tin-oxide conducting substrate with PEDOT layer sequencing followed gold contact for extracting charge carriers referring to appropriate band energy level diagram elucidate solar-cell type, behavior due easy charge transportation process of holes and electrons in a different direction of heterojunction. Despite a low power conversion efficiency due to weak current density and voltage.

Keywords: Heterojunction; n-CdSe/p-Cu$_2$Se; Solar Cells; Electrodeposition.
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1. Introduction

Nowadays, energy consumption is a major crisis across the world. The human lifestyle being a matter of power is a well-known fact in economically backward countries with the availability of limited conventional power sources.[1] The discovery of a *p-n* junction Si photovoltaic (PV) device in 1954 has made world breakthrough.[2] Many transparent *n*-type semiconductor films such as SnO$_2$,[3] In$_2$O$_3$,[4] indium-tin-oxide,[5] CdSe[6] and CdS[7] as window materials can be deposited on *p*-type semiconductors for obtaining various heterojunction-type PVs. In contrast, few materials are showing as well as *p*-type conduction mechanisms. Cuprous chalcogenides such as Cu$_2$S, Cu$_2$Se, and Cu$_2$Te typically endow *p*-type behavior and are highly conductive and semi-transparent. The Cu$_2$S [8] and Cu$_2$Te[9] are generally prepared by the chemical reaction of copper with CdS, CdSe, and CdTe. The Cu$_2$Se is also considered as a suitable candidate for forming a heterojunction with a n-type semiconductor which is highly conductive and easy to prepare.[10-12,51] In heterojunction solar cells, the part of the cell serves as a window must have the moderate forbidden gap in addition to a very low resistivity.

In some heterojunction solar cells, CdS is successfully envisaged window layer material.[11-22] Since CdS exhibited high band gap of 2.4 eV and a very low resistivity up to 10^{-2} Ω cm. One can design an effective and efficient heterojunction solar-cells, by using CdSe or CuSe as absorbers with suitable band level alignments obtained for various ‘x’ values. The power conversion efficiency of PV cells can be increased with the introduction of the donor-acceptor hetero-junction that serves to dissociate strongly bound photo-generated excitons[23] where barrier-free charge transportation is achieved by forming *n*-type semiconductor layer of relatively lower conduction and valance band positions than *a p*-type semiconducting layer. Therefore, the study of II-VI and I-VI polycrystalline thin films have been increased, due to a tremendous surge of interest in potential applications such as thin film transistors, IR detectors, lasers and photovoltaic

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devices.[29] Polymer-based organic-inorganic PV devices have attracted enormous interest in recent years due to their low fabrication cost, ease of processing, and mechanical flexibility on bonding nanocrystalline semiconductors of the high density of electronic states the charge transfer rate can be remarkably engineered.[24]

Various studies in the literature have demonstrated organic-inorganic hybrid hetero-junction PV devices.[25,26] In such structures, almost all excitons formed are dissociated at the organic-inorganic interface *via* a hole and electron transfer to produce free charges. All charge carriers have pathways to the connecting electrodes, through the organic-inorganic boundary, and their transfer facilitates when polymer chains are aligned to increase their charge carrier mobility. The maximum increment of a donor-acceptor regime is essential to enhance the efficiency of exciton generation, dissociation, and charge transportation. In this work, we present simple, reproducible, low-temperature and cost-effective electrodeposition technique to achieve low-cost heterojunction solar cells. Here n-cadmium selenide and p-copper selenide (*n*-CdSe and *p*-Cu_2Se) were employed in heterojunction formation and the heterojunction is subjected to photoelectrochemical studies.

2. Experiment

2.1 Substrate Cleaning:

The indium-tin-oxide (ITO) slides of 10 ohm-cm resistivity, purchased from SAMSUNG ELECTRONICS, were used as substrates. The procedure adopted for cleaning these pieces were an ultrasound cleaning *i.e.* they were initially washed with soap water then ultrasonically cleaned for 10 minutes in double distilled water, and10 minutes in anhydrous ethanol solution which finally were dried and degreased in AR grade acetone before use.

2.2 CdSe Electrodeposition

The electrodeposition (ED) of CdSe films was carried out in an acidic electrolyte bath containing 0.05 M $CdSO_4$ aqueous solution (6 ml) and an equal volume of 0.01 M SeO_2 maintained at 300 K. The distance between anode and cathode was fixed to 0.5 cm. The spiral platinum (Pt) wire electrode was used as an anode *i.e.* counter electrode. The ED was carried out under galvanostatic mode in the presence of (Ag/AgCl) electrode as a reference whose tip was fixed at 2 cm distance from the cathode. The constant current density of 2 mA/cm^2 was applied between the ITO-working and Pt-counter electrodes. The pH of the resultant solution was ~3-4. Different samples were prepared by varying deposition periods such as 500, 1000, and 1500s, respectively and then, the as-obtained CdSe films were annealed for 1 hour at different annealing temperatures, *i.e.* 373, 473 and 573 K to improve the crystallinity.

2.3 Cu_xSe Electrodeposition

The ED of Cu_xSe films was carried out in an electrolyte bath containing 0.01 M $CuSO_4$ aqueous solution (25 ml) and an equal volume of 0.01 M SeO_2 was dropwise added under constant stirring maintained at 300 K. The distance between the anode and cathode electrodes was fixed to 0.5 cm. The spiral platinum (Pt) wire electrode was used as an anode. The ED was performed under a potentiostatic mode using a constant voltage source (0-10 V) in the presence of the Ag/AgCl reference electrode was located within 2 cm distance from the ITO, working electrode. The constant current density of 1mA/cm^2 was applied between the ITO working and Pt counter electrodes. Cu_xSe films of different thicknesses obtained by varying deposition periods of 500, 1000, and 1500 s which were annealed for 1 hour at different annealing temperatures, *i.e.*, 373, 473 and 573 K to improve the crystallinity.

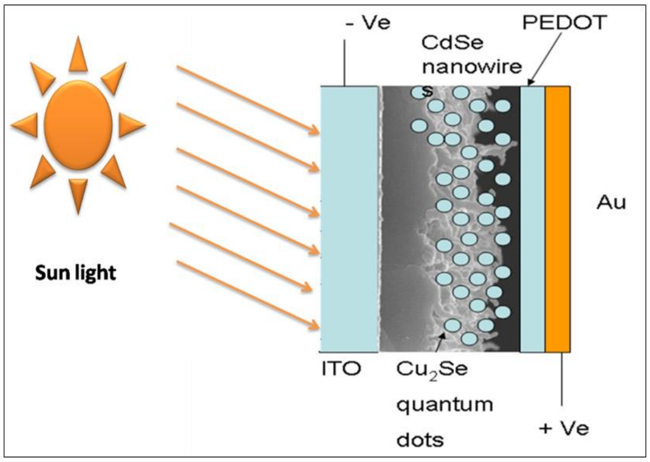

Fig. 1 Schematic presentation of CdSe/Cu2Se hetero-junction solar cell, where Cu_2Se quantum dots are linked to CdSe nanowires.

2.4 n-***CdSe***/p-***Cu_2Se*** heterojunction solar cells

The deposition of the one layer can be easily obtained by a variety of methods but a major problem is to form the second layer without disturbing the first one. During this process, the ions of the first layer can be easily exchanged with the ions of the second layer depending on the chemical stability.[27] Therefore, there is a strong chance to remove the initially deposited layer. We have formed stable solution-based *p-n* junction solar cell where CdSe is *n*-type and Cu_2Se is an extrinsic *p*-type semiconductor. The *n*-type CdSe and *p- type* Cu_2Se layer in the form of the nanowire quantum dots

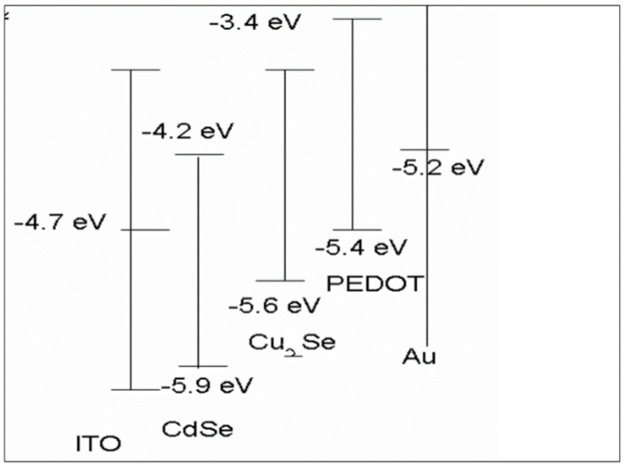

Fig. 2 Energy levels diagram for CdSe and Cu_2Se with respect to ITO and PEDOT (vacuum level).

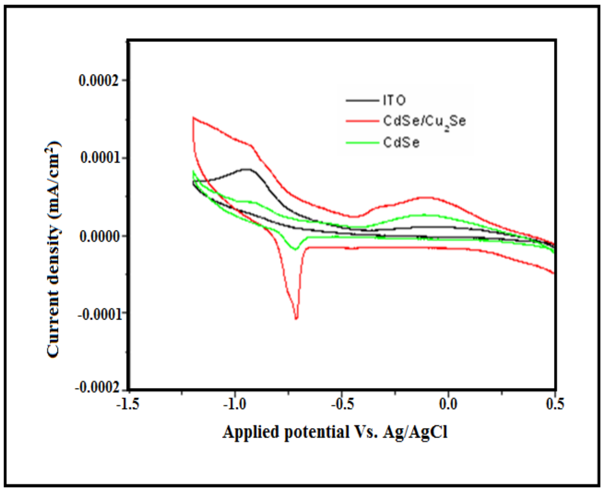

Fig. 3 The cyclic-voltammograms of CdSe and CdSe/Cu_2Se.

layer was obtained by the electrodeposition method. The deposition time was selected to be 1500 s and the obtained films were annealed at 473 K after every deposition. The Cu_xSe quantum dots were linked to CdS nanowires using electrodeposition and then a thin PEDOT (poly-ethylene dioxythiophene) layer was applied on it for easy transport of hole as PEDOT is good hole scavenger.[52] The device structure as shown in Fig. 1 consists of ITO film, CdSe nanowires, Cu_xSe quantum dots, PEDOT layer followed gold contacts which are linked to CdSe nanowires. Fig. 2 illustrates the energy band diagram for CdSe and CuxSe hetero-junction where the charge transport of electrons to ITO from CdSe nanowires and holes to PEDOT due to aligned energy levels can be plausible. These energy levels were estimated using Fig. 3 cyclic-voltammetry curves and corresponding bandgap energies, obtained from optical studies. Lower conduction band (-4.2eV) and valence band (-5.9 eV) positions of CdSe nanowires enable easy transport of photoelectrons obtained from exciton separation at Cu_xSe quantum dots and CdSe nanowire interfaces.[3,4,30]

The electrochemical reactions for the formation of CdSe and Cu_2Se are as follows,

$$SeO_2 + H_2O \rightarrow H_2SeSO_3$$

$$3\ Cd^{2+} + H_2SeSO_3 + 4\ H^+ \rightarrow CdSe + 2\ Cd^{2+} + 3\ H_2O$$

$$Cu^{2+} + SeO^{2-}_3 + 6H^{+} + 6\ e^- \rightarrow CuSe + 3\ H_2O$$

$$Cu^{2+} + CuSe^{+}\ 2\ e^{-} \rightarrow Cu_2Se$$

3. Characterization

The as-deposited CdSe and Cu_xSe films were characterized for their structure and optical properties using X-ray diffraction

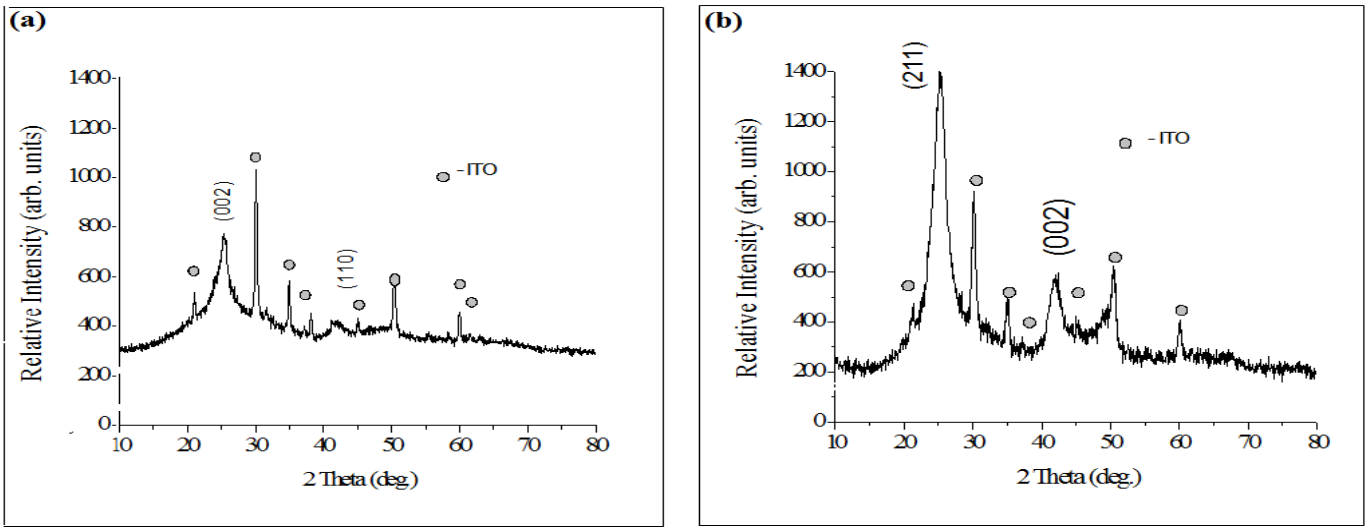

Fig. 4 The XRD pattern of (a) CdSe film fabricated from the acidic bath for 1500s deposition time and annealed at 473 K for 1 h (b) Cu_2Sefilms deposited for 1500 s deposition period and annealed at 473 K for 1 h.

(XRD) and ultraviolet-visible absorption measurement techniques, respectively. The surface morphologies of the as-prepared films were recorded using a scanning electron microscopy digital photo images. Water contact angle measurements were formed over CdSe and Cu_2Se films for confirming surface wettability *i.e.*, surface energy.

4. Results and Discussion

4.1 Structural elucidation

Fig. 4 (a) shows the XRD pattern of CdSe where a broad hump at ~25° in accord to the formation of nanocrystalline structure. This position corresponds to the (002) plane of cubic CdSe (powder Diffraction File no. 88-2346), suggesting the unidirectional growth of CdSe *i.e.*, along c-axis.[31,32] This observation suggested that depending on the deposition time, structure changes from amorphous to nanocrystalline.[32] The average crystallite size was calculated using the following relation.[33, 34]

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where, D is the average crystallite size, β is the angular width in terms of 2θ, *i.e.*, FWHM. The average crystallite size of 45 nm was estimated for CdSe films fabricated from an acidic bath for 1500 s and annealed at 473 K for 1 h. Fig. 4 (b) shows the XRD pattern of Cu_2Se films composed of quantum dots, which were obtained for 1500s deposition period and annealed at 473 K for 1 h. The XRD peaks are well matched with standard diffraction data file nos. 37.1187 and 47.1745, revealed the growth of Cu_2Se phase. The Increase in crystallinity of the films is attributed to the process of re-crystallization as increase in deposition time which results into the change of structure from amorphous structure to crystalline.[28] Films of Cu_xSe were relatively thick and polycrystalline. From the XRD study, nanocrystalline and polycrystalline structures of the CdSe and Cu_2Se were separately identified.

4.2 Surface appearance

The surface morphology of the CdSe films deposited for the deposition time of the 1500 second is composed of nanowires. Fig. 5 (a, b) shows the SEM images of CdSe and Cu_2Se films respectively. Nanowires of CdSe were uniformly distributed over a complete surface area used for scanning as shown in Fig. 5 (a). These nanowires were of ~ 40 nm in length and few microns in length. Due to twisted and one another indulged ends one not fixed the exact length of the individual nanowire. Therefore, the thickness of the film was considered as the length of the wire. Furthermore, enhancement in both the diameter and length of the CdSe nanowires was confirmed concerning the deposition time, indicating that the surface morphology of the CdSe films is strongly correlated with the amount of CdSe deposited, which is a function of deposition time.[32] The spherical surface morphology of the Cu_2Se film deposited for the 1500 s and annealed at 473 K from an acidic bath investigated from the SEM image is shown in Fig. 5 (b). Uniformly distributed, densely packed spherical grains of Cu_xSe were clearly observed over the substrate surface.

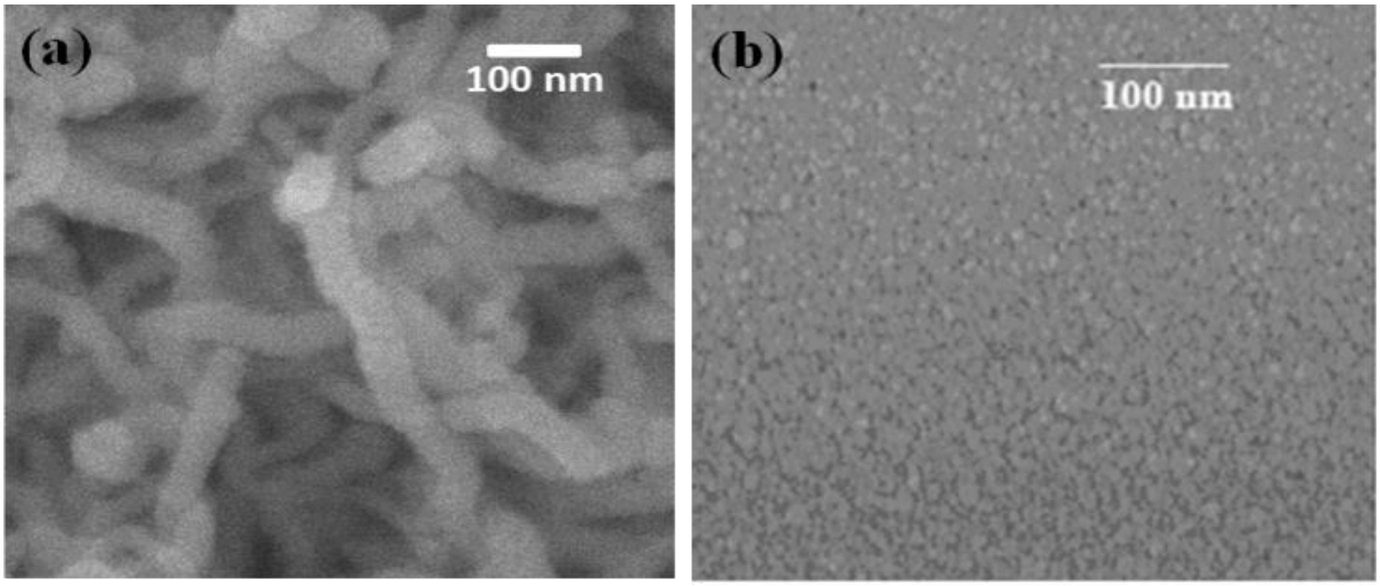

Fig. 5 (a, b) The SEM surface image acidic CdSe film deposited for 1500 s and annealed for 1 h at 473 K in air and that of acidic Cu_2Se films deposited for 1500 s and annealed at 473 K in air for 1 h.

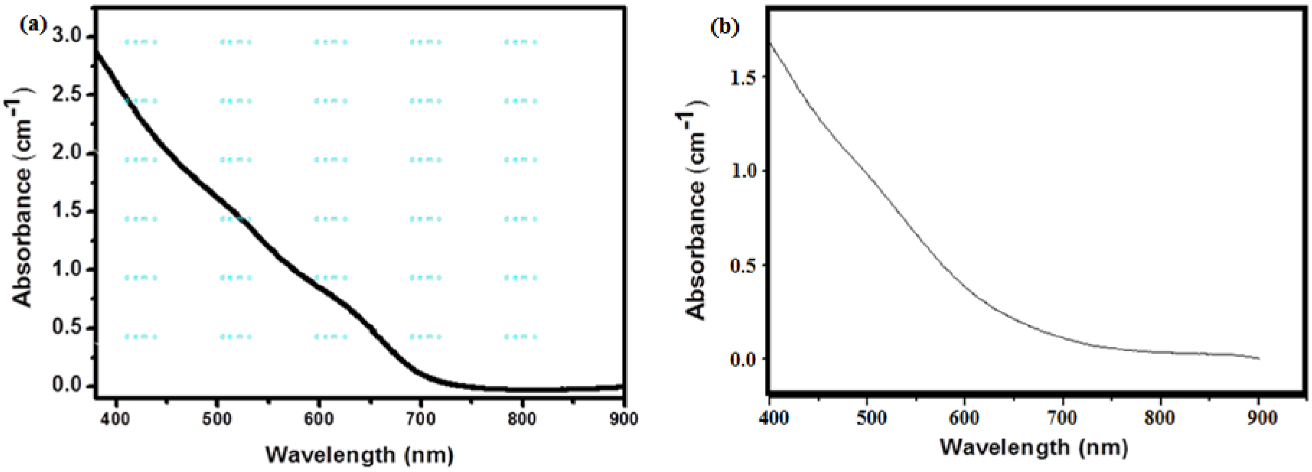

Fig. 6 Plot of absorbance against wavelength for CdSe (a) and Cu_2Se (b) films in the acidic bath for 1500 s deposition periods and annealed for 1 h at 473 K.

4.3 Optical measurement

Optical absorbance was considered for estimating the bandgap energy and corresponding conduction and valence band levels. The optical of CdSe nanowires was investigated by using UV–vis spectrophotometer in the wavelength range of 400-800 nm. The plot indicated that the CdSe film deposited for the 1500 s was bearing a relatively high degree of optical absorption and showing absorbance in-between 700-800 nm. We estimated the bandgap energy of 2.08 eV due to its nanocrystalline character.[35] The absorption band edges fitted to a direct transition for fractions 1 and 4 are shown in Fig.6.[35] The bandgap widening in the CdSe films is attributed to; a) change in morphology, and b) increase in the overall thickness of the film with deposition time.[36] It is well known that the CdSe is perfect absorbent with an absorption edge at 700 nm.[37] For annealed films, absorbance increased slightly which is a common observation for semiconducting metal chalcogenide/oxide films.[38-41] The optical absorbance spectrum of Cu_xSe films deposited for 1500 s deposition periods and annealed for 1 hat 473 K from the acidic bath is shown in Fig. 6 (b). From the plot, the bandgap energy of 2.3 eV was estimated which is higher than CdSe. The higher bandgap energy material acts as a window layer by passing the photons of low energy to the material commonly known as the absorber layer.

4.4 Surface wettability

To have good interfacial contact, hydrophilicity should be matched well *e.g.* hydrophilic surface can have a good interface with hydrophobic and vice-versa on the other hand two hydrophilic or hydrophobic surfaces cannot show well interfacial contacts. Fig. 7 (a, b) shows the water contact angle

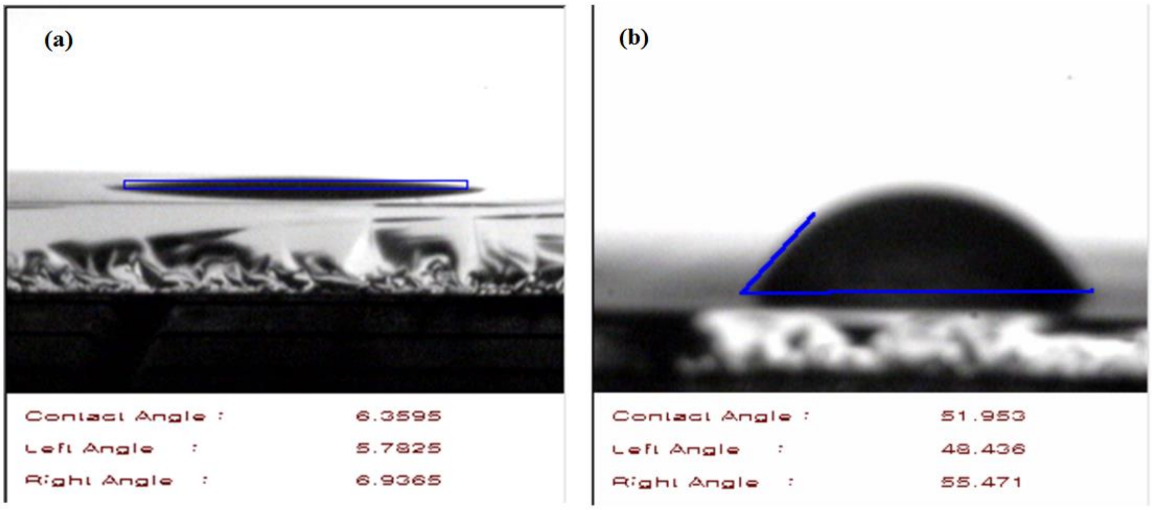

Fig. 7 Water contact angle measurements on (a) CdSe and (b) Cu_2Se film surfaces fabricated.

measurement on CdSe film surface fabricated for the 1500 s in the acidic bath which is close to 6.36° supporting that the CdSe nanowires morphology is super-hydrophilic, suggesting that the CdSe can form a good contact line at the interface between solid, liquid and air.[42–45] On the other hand, the water contact angle measurement on the Cu_xSe film surface deposited for the 1500 s from an acidic bath is relatively hydrophobic with a water contact angle measurement of 52°. Therefore, our selected inorganic materials can provide good interfacial contact from a wettability point of view.

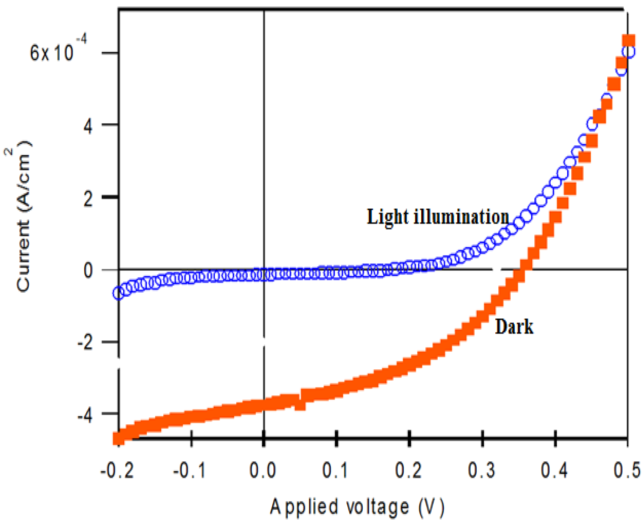

Fig. 8 Performance of CdSe- Cu_2Se solid-state heterojunction solar cell device.

4.5 Hetero-junction solar cell performance

We explored CdSe nanowires/Cu_xSe quantum dots followed by PEDOT and Au contacts as a solid-state solar cell device. Here, PEDOT was used to ensure good electrical contact governed by easy hole transportation. Fig. 8 shows the current density-applied voltage (J-V) curves under the dark and the light illumination of the CdSe-Cu_xSe PV device under a light intensity of 80 mW/cm^2. The light was exposed from the ITO side as PEDOT is not permitting it to fall on the absorber CdSe layer. From the current-voltage curves, fill factor (*FF*), power conversion efficiency (η %), short circuit current, open-circuit voltage were obtained. Presented *n*-CdSe/*p*-Cu_2S solid-state solar cell device showed a power conversion efficiency of 0.67 % which is interesting and higher than reported for only CdSe/P_3HT solid-state solar cells reported elsewhere.[46] Moreover, the electron transport can be more efficient for the nanowires due to their longer electron diffusion lengths in contrast to percolation through the spherical nanoparticles (crystallite edges generally forms recombination centers).[47–50] PV cell revealed a short circuit current of about 0.4 mA/cm^2, the open-circuit voltage of about 0.35 V, and fill factor of 47%. The small value of the fill factor is due to the combination of series resistance and resistance caused by Cu_xSe quantum dots and CdSe nanowire interfaces.

5. Conclusion

In this work, the n-CdSe/p-Cu_xSe hetero-junction was designed and tested for surface morphology, crystal structure, and bandgap. The device structure consists of ITO film, CdSe nanowires, Cu_xSe quantum dots, PEDOT hole scavenging layer followed by gold contacts for electrical connections. Using band energy level diagram transportation of photoexcited electrons and hole is illustrated. Favorable band alignment of CdSe and Cu_2Se has enabled easy transportation of charge carriers across the interface. From the current-voltage curves, fill factor (*FF*), solar to electrical power conversion efficiency (η%), short circuit current, the open-circuit voltage was obtained. Present CdSe/Cu_xSe solid-state solar cell has approved a poor power conversion efficiency of 0.67% which needs to be improved either by engineering interfacial layer or on doping fast charge transport materials that endow smaller charge transfer resistance.

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Supporting Information

Not applicable

Conflict of interest

There are no conflicts to declare.

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