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# Solution processed hole transport layer towards efficient and cost effective organic solar cells

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ABSTRACT

In this work, we report Copper Sulfide (CuS) as a solution processed, inexpensive and effective hole transport layer (HTL) for efficient and low cost organic solar cells. These devices were fabricated using two most studied low band gap donor materials PTB7 and PCDTBT blended with $PC_{71}BM$ as an acceptor material. We have used a simplest device architect such as ITO/CuS/active layer/Al at ambient conditions. The power conversion efficiencies (PCEs) of these devices have been achieved to up to 4.32% and1.76 % for PTB7 and PCDTBT based devices respectively. Finally, we have provided a further example of solution processable CuS as an effective HTL for solution processable organic photovoltaic applications.

## 1. Introduction

Organic photovoltaic (OPV) cells have drawn great scientific attention over the last few years, due to its potential to produce flexible, light weight, low cost solar cells using organic materials. However, the power conversion efficiency achieved for these systems is low for extensive implementation of the technology. Among the various photovoltaic technologies, organic/polymer photovoltaic based on solution processed bulk-heterojunction (BHJ) concept gained significant attention due to the use of inexpensive light-weight materials, exhibiting high mechanical flexibility and compatibility with low temperature roll-to-roll manufacturing techniques (Krebs et al., 2014; Li et al., 2014). In OPVs, especially in bulk heterojunction organic solar cells (OSCs) consist of many components such as electrodes (anode/cathode); interface layers (IFLs) and active materials (donor/acceptor). Each and every component has its own importance and functionality. Interface layers play a very important role in collection and extraction of the charge carriers, these layers are inserted between electrodes (anode/cathode) and active layer interface (Khodabakhsh et al., 2004; Tokmoldin et al., 2009). To moderate the charge carrier recombination at the electrodes, various interface layer (IFL) materials have been developed to selectively allow desired charge carriers to pass through and block undesired carriers. Therefore, charge carrier recombination at electrodes can be substantially suppressed and PCEs can be significantly improved for the cells with engineered IFLs. Hole transport layer (HTLs) and electron transport layer (ETLs) are part of Interface layers.

In the field of organic solar cells (OSCs) a number of materials were used as HTLs, out of them solution processable materials are most prefer choice. PEDOT:PSS is a most successfully used solution processed HTL due to its high conductivity, transparency and suitable work function (Zhang et al., 2002; Li et al., 2005). But due to hygroscopic, acidic and protonation nature of PSS influences the device stability (Wong et al., 2002; Kemerink et al., 2004) and degradation due to these limitations hole transport layer PEDOT:PSS replaced by the several inorganic materials and organic materials. In inorganic materials, Transition metal oxides were also used, these materials have air stability and high optical transparency but due to insolubility in most of the common solvents, these materials are usually deposited by vacuum deposition technique (Irwin et al., 2011), which is incompatible with the concept of low cost OSCs fabrication. To overcome the problem of vacuum deposition of inorganic materials the preference comes to solution processable approach. Several solution processable methods were reported by using different inorganic precursors (Girotto et al., 2011), nanoparticles (Stubhan et al., 2011), colloidal particles (Steirer et al., 2010) etc. In recent years, more and more solution processable metal oxides, such as $CuO_x$ (Xu et al., 2013), $MoO_3$ (Tan et al., 2013), $ReO_x$ (Tan et al., 2014), $VO_x$ (Tan et al., 2012), $NiO_x$ (Wong et al., 2012), $SnO_x$ (Trost et al., 2012), $WO_3$ (Tan et al., 2012) and $RuO_x$ (Wang et al., 2014) etc have been used for stable OSCs. Out of these copper based materials like copper iodide (CuI) and copper thiocyanate (CuSCN) Gross et al., 2014 have recently emerged as other effective and robust inorganic hole transport materials for OSCs. CuI and CuSCN are highly transparent and efficient HTL for organic solar cells but these materials required selective solvents to dissolve which is very expensive

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and bad smelly because of these reasons we required inexpensive, easily soluble in common solvents and stable hole transport material for low cost and efficient OSCs fabrication. Various nanostructures of $CuS/Cu_2S$ (Kamazani et al., 2016), $CuInS_2$ (Kamazani et al., 2015a, 2015b) and $CdIn_2S_4$ (Kamazani et al., 2016; Kamazani and Niasari, 2017) were chemically synthesized and used in dye-sensitized solar cells (DSSCs) as a barrier layer. Copper Sulfide was also used as a counter-electrode (Congiu et al., 2016) in DSSCs and quantum dot-sensitized solar cells (Xia et al., 2016) by magnetron sputtering (Wang et al., 2016) method.

In this series we have reported, CuS as a solution processed, low cost, robust and easily available HTL layer which used in organic solar cells, gives the better efficiency as compare to well known and conventionally used solution processed HTL material PEDOT:PSS.

## 2. Experimental

### 2.1. Reagents and materials

The donor materials Poly[N-9″-hepta-decanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole) (PCDTBT), Poly[[4,8-bis[(2-ethylhexyl)oxy]Benzo[1,2-b:4,5-b′]dithiophene-2,6-diyl][3-fluro-2-[(2-ethylhexyl)carbonyl]thieno[3,4-b]thiophenediyl]] (PTB7) and acceptor material Phenyl-$C_{71}$-butyric acid methyl ester ($PC_{71}BM$) were purchased from Ossila Ltd, England. Copper Sulfide (CuS) and different solvents used in this study such as 1,2-dichlorobenzene (DCB), Chlorobenzene (CB), Diiodooctone (DIO) were obtained from Sigma Aldrich.

### 2.2. Preparation of active layer and HTL solutions

In this study, two well known active layer combinations were used for device fabrication. Electron donor material PCDTBT and electron acceptor material $PC_{71}BM$ were weighed (1:4 w/w) and dissolved in mixed solvents of chlorobenzene (CB) and 1,2-dichlorobenzene (DCB). Other donor-acceptor combination PTB7:$PC_{71}BM$ (Ouyang et al., 2015) were weighed (1:1.5 w/w) and dissolved in chlorobenzene with DIO. Both active layer solutions were stirred for 12 h inside the glove box. The optimized concentration of CuS (7mg/ml) was weighed out, put in DMF solvent and sonicated for overnight after that we take clear solution for HTL deposition.

### 2.3. Process of device fabrication

All devices were fabricated on ITO coated glass substrates. ITO coated substrates were patterned using laser ablation technique. The patterned ITO coated substrates were cleaned in sequential with acetone, methanol and isopropanol, followed by drying for 20 min. After that the CuS HTL clear solution in DMF was take it out and spin coated on cleaned ITO substrates at 3000 rpm for 60 s, annealed at 100 °C and then dries for 1 h. The other well known solution processed HTL layer, PEDOT: PSS were deposited by spin coating with spin speed of 2000 rpm and annealed at 120 °C. The active layer solutions were spin-coated onto the HTL layer with spin speed of 1000 rpm for 90 s and annealed at 70 °C on a hot plate. Finally, the devices were completed by thermally deposited Al as cathode electrode at base pressure of $10^{-6}$ Torr.

### 2.4. Thin film and device characterization

The optical absorption and transmission of CuS thin film was measured by using UV-1800 Shimadzu spectrophotometer and the surface morphology of CuS film in DMF solvent on ITO substrates was acquired by using atomic force microscopy (AFM) NT-MDT Solver Pro. The current density–voltage (J–V) characteristics of fabricated devices were measured using a computer controlled Keithley 2400 source meter under dark and illumination conditions.

## 3. Results and discussions

### 3.1. Optical measurements

Absorption spectrum of solution processed CuS film in DMF solvent was recorded on ITO substrates to investigate the absorption across the range of solar spectrum. CuS shows the absorption in the UV-region around < 500 nm, clearly shown from Fig. 3(a).

Therefore, it is clear that the CuS film shows significantly lower parasitic absorption which makes is an efficient hole transport layer for OSCs additional it improve the power conversion efficiency (PCE). Similarly, in transmission spectra of CuS film in DMF solvent on ITO substrates shown in Fig. 3(b). The CuS film show high transparency in the range of 300 to 1000 nm, it exhibits high transparency around ~84%, which is comparable to PEDOT:PSS and other transition metal oxides. High transparency of CuS (HTL) film make potential candidate as a hole transport layer for OSCs.

To study the usefulness of CuS as a potential solution processed HTL material for OSCs, we consider conventional device structure ITO/HTL/active layer/Al shown in Fig. 1. Two most studied low band gap donor polymers PTB7 and PCDTBT blended with $PC_{71}BM$ were used as active layer for device fabrication (see Fig. 2.).

### 3.2. Photovoltaic device characteristics results

To study the performance of CuS as an HTL, we have fabricated OSCs devices with device structure ITO/CuS/active layer/Al. For better device performance first, the concentration of CuS solution was optimized followed by the thickness of the HTL after that the optimized concentration used for further study. For comparison with CuS HTL devices, we have also fabricated reference OSCs devices using PEDOT:PSS as a HTL in same environmental conditions. Fig. 4, shows the current density-voltage (J-V) characteristics of PEDOT:PSS reference devices using PTB7:$PC_{71}BM$ and PCDTBT:$PC_{71}BM$.

After that, we have recorded the current density-voltage (J-V) characteristics of CuS based devices using PTB7:$PC_{71}BM$ and PCDTBT:$PC_{71}BM$ shown in Fig. 5(a) and (b).

The OSC devices with CuS exhibit highest PCE with PTB7:$PC_{71}BM$ PCDTBT:$PC_{71}BM$ combinations are 4.32% and 1.76 respectively as presented in Table 1. However the reference devices with PEDOT:PSS show lower PCE as compare to reference devices of around 2.48% and 1.41% with PTB7:$PC_{71}BM$ PCDTBT:$PC_{71}BM$.

It was observed that under identical conditions all the devices show good performance, while the CuS HTL was deposited with DMF solvent as a HTL material exhibits best results as compared to reference devices with active layer combinations. Which is clearly shown from Table 1.Interestingly, we have found that HTL CuS has significant effects on FF. Which is major reason behind improve the PCE of CuS

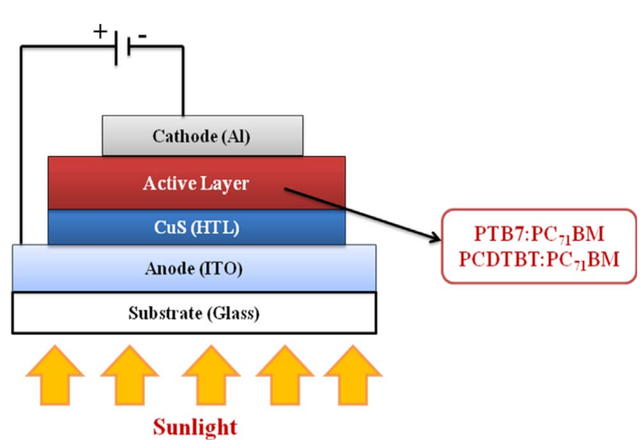


**Fig. 1.** Schematic organic solar cell devices with CuS as a hole transport layer.