COPPER IODIDE AS THE HOLE TRANSPORT LAYER IN BULK HETEROJUNCTION ORGANIC PHOTOVOLTAICS

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INTRODUCTION

Polymer solar cells undoubtedly hold tremendous potential for solution-processable, inexpensive photovoltaics on flexible plastic substrates (Shaheen *et al.*, 2005). The most promising organic photo voltaics (OPVs) are based on random dispersion of acceptors in the form of organic or inorganic nanostructures within a conjugated polymer matrix, which acts as the donor phase. The interfaces at the acceptor nanostructures and the donor host polymer matrix create bulk heterojunctions (BHJs), which provide a large number of sites for charge separation and continuous pathways for efficient carrier transportation (Duren *et al.,* 2004). Although numerous combinations of acceptors and donors have been reported, the most popular BHJ polymer solar cells consist of poly(3-hexylthiophene) (P3HT) and fullerene derivative phenyl-C61-butyric acid methyl ester (PCBM) blends. The mechanisms for achieving high photovoltaic efficiencies in excess of 6% in P3HT:PCBM BHJ devices are well established (Ma *et al.,* 2005). However, several key components remain unresolved and must be addressed if the theoretical efficiency of 10% is to be reached (Dennler *et al.*, 2009). For example, in a simple BHJ device, both the donor and acceptor phases are in direct electrical contact with the cathode and anode electrodes, leading to recombination of charge carriers and current leakage. To minimize such detrimental effects, electron blocking and hole transport layers (HTLs) are deposited on top of the transparent and conducting tin oxide (CTO) anode. HTLs must be wide band gap p-type materials, and several inorganic materials such as V_2O_5 and MoO_3 (Shrotriya *et al.,* 2006) have been reported with NiO being the most effective, attaining efficiencies greater than 5% (Irwin *et al*, 2008). However, inorganic HTLs are deposited using vacuum deposition techniques that are incompatible with the advantages of solution-processable and printable electronics of OPVs. Thus, the most commonly employed HTL in polymer solar cells is semiconducting poly 3,4-ethylene dioxythiophene: polystyrene sulfonic acid (PEDOT:PSS) between the ITO anode and the active layer. PEDOT:PSS has the advantages that it is deposited from solution and serves to minimize the detrimental effects of CTO roughness as well as to align the work functions of P3HT and CTO for more efficient collection of holes. However, PEDOT:PSS is usually deposited from highly acidic (~ pH 1) aqueous suspensions that are known to corrode CTO at elevated temperatures (Kim *et al.,* 2006) and can also introduce water into the active layer, degrading the device performance (Lagemaat *et al.,* 2006). Our research is motivated by the need to overcome the limitations of PEDOT: PSS as the HTL by finding a suitable solution-processable alternative that is compatible with OPV materials and fabrication techniques. Therefore this research attemptedfocused to find out solution-processable HTL materials purely soluble in organic solvents to mitigate the inclusion of water into the active layer which occur with the use of PEDOT:PSS.

Copper Iodide (CuI) is an inorganic p-type high band gap hole conducting material. In fact it is easily soluble in organic solvents such as acetonitrile. Moreover, the hole mobility of CuI is quite high and band positions fit well with the HOMO and LUMO levels of the active materials (P3HT:PCBM) of the OPV for efficient transport of holes to the CTO. Further it has been reported to be used as hole transport materials in dye sensitized solid state solar cells as well. Thus in this work we report the use of thin films of CuI as HTL in OPVs which minimize the back electron transfer enhancing the efficiency of the cell.

METHODOLOGY

Conducting tin oxide (CTO) glass plates were used as the substrates for the deposition of active materials after cleaning by sonication in propenol for 15 minutes. 50 mg of CuI dissolved in 2 ml of acetonitrile was used to deposit the HTL on these substrates by spin coating at 2500 rpm. To prepare the active layer, 20 mg of P3HT and 15 mg of PCBM were dissolved in 1 ml of chlorobenzine by stirring for 3 hours. Then the active layer, P3HT:PCBM of thickness around 200 nm – 400 nm was deposited by following the same technique. The films were kept on a hot plate at 80 °C for 5 minutes. Silver paste was applied on the top of the P3HT:PCBM layer to make the back contact.

The organic polymer materials used were characterized by UV-Visible spectroscopy. The BHJ OPVs were characterized by I-V and impedance spectroscopic measurements.

RESULTS AND DISCUSSION

Figure 1 shows the UV-visible spectra of (a) P3HT (b) PCBM and (c) P3HT:PCBM blend in chlorobenzine that used to deposit the active layer of the organic photovoltaic cells. As it is evident from the figure the polymeric material, P3HT is solely responsible for the absorption of light in the visible region. The polymeric material, PCBM only absorb light in the ultraviolet region. Thus OPVs become active for both the UV and visible light by combining the two materials together.
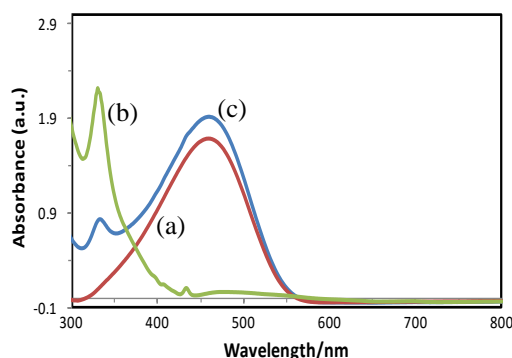

Figure 1 UV-Visible spectra of (a) P3HT (b) PCBM and (c) P3HT:PCBM blend

Figure 2 illustrate the heterostructure CTO/CuI/P3HT:PCBM/Ag of the OPV. In order to compare the photo response of the above device structure, the heterostructure of CTO/PEDOT:PSS/P3HT:PCBM/Ag was also fabricated with spin coating PEDOT:PSS under the same condition which used to deposit CuI layer.
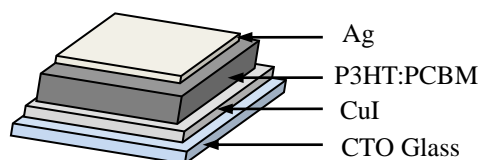

Figure 2: Schematic diagram of a heterostructure of CTO/CuI/P3HT:PCBM/Ag of the OPV

I-V characteristic curves of the BHJ solar cells of the structures (a) CTO/CuI/P3HT:PCBM/Ag and (b) CTO/PEDOT:PSS/P3HT:PCBM/Ag are depicted in figure 3. The cell parameters such as short circuit photocurrent (J_{sc}), open circuit photovoltage (V_{oc}), fill factor (FF) and efficiency (η) are given in Table 1 that measured under the illumination of 100 mWcm^{-2} for comparison. The efficiency of the CTO/CuI/P3HT:PCBM/Ag cell is around

0.1% which is not significant compared to the current records of BHJ solar cells with PEDOT:PSS as hole transport layer. However, the higher photovoltage of the cell assures that the band structure of CuI is well matched with the other organic semiconductors for efficient transfer of electrons and holes. The low photocurrent of this cell may be due to the low work function of silver paste where aluminum is the back contact normally for BHJ solar cells which is deposited by physical vapour deposition.
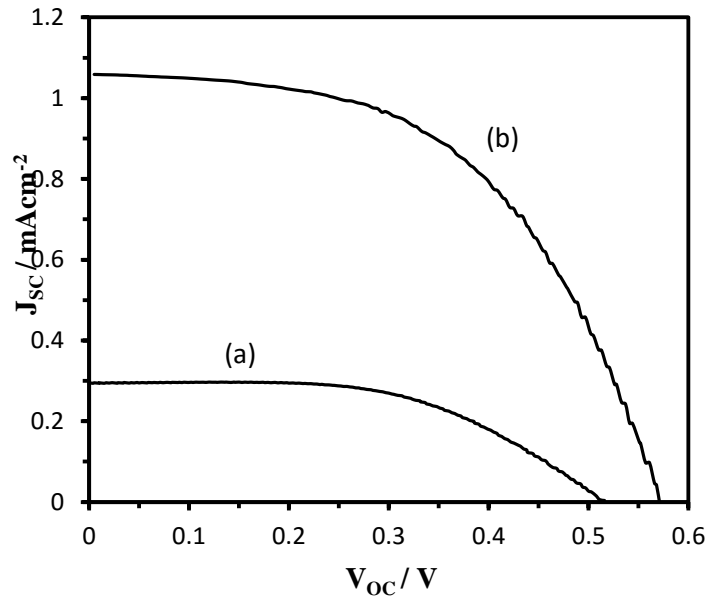

Figure 3: I-V characteristic curves of the BHJ solar cells (a) CTO/CuI/P3HT:PCBM/Ag and (b) CTO/ PEDOT:PSS /P3HT:PCBM/Ag.

Table1: Cell parameters of CTO/CuI/P3HT:PCBM/Ag and CTO/PEDOT:PSS/P3HT:PCBM/Ag BHJ solar cells measured under 100 mWcm^{-2} illumination.

Heterostructure of the Device	Jsc (mAcm^{-2})	Voc (V)	FF %	η%
CTO/CuI/P3HT:PCBM/Ag	0.295	0.516	54	0.08
CTO/PEDOT:PSS/P3HT:PCBM/Ag	1.058	0.568	53	0.31

Impedance spectroscopy (IS) is used to study the dielectric properties of a medium as a function of frequency. Therefore the frequency response of the system reveals the electrical energy storage and dissipation properties where the data obtained by IS are expressed graphically in Nyquist plot.

Equivalent circuit could be modeled for such an impedance spectra and resistance and capacitance values of the circuit components of the system can be found out by analysis. Figure 4 shows the impedance curves for the heterostructures CTO/CuI/P3HT:PCBM/Ag and CTO/PEDOT:PSS/P3HT:PCBM/Ag. It is clear from the Nyquist plots that the CuI based heterostructure has a high parallel resistance (4500 kΩ) than the PEDOT:PSS based cell (12 Ω). This may be also a reason for the low photocurrent of the CuI based OPV. But it is possible to dope CuI films to gain high conductivities with I$_2$ and other elements which may improve the cell performance.

CONCLUSIONS/RECOMMENDATIONS
A possible bulk heterojunction OPV was developed using CuI as the hole transport layer. Since the fabrication was done solely by solution processable technique using non-aqueous solvents, the stability of the device needs to be tested for any improvement. The performance of this cell is inferior to the current BHJ OPVs developed with PEDOT:PSS hole transport layer due to several reasons. The reasons are non usage of expensive vacuum deposited

aluminium back contact and the high parallel resistance of the OPV based on CuI which could be overcome by doping the CuI layer.

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