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Low band gap polymeric solar cells using solution-processable copper iodide as hole transporting layer

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ABSTRACT

In the present work, we have shown the performance of solution-processable copper iodide (CuI) as an alternative hole transporting layer (HTL) for polymeric solar cells. Optical spectra of the CuI thin film reveal highly transparent and practically no absorption in the range vis-NIR region (450–1110 nm). X-ray diffraction (XRD) patterns of CuI exhibits as a *p*-type semiconductor as well as crystalline nature. The photovoltaic devices were fabricated using PCDTBT and PTB7 as donor materials blended with $PC_{71}BM$ as an acceptor material. The power conversion efficiencies (PCEs) based on CuI as an HTL have been achieved to up to 3.04% and 4.48% for PCDTBT and PTB7 based donor materials respectively with a configuration based on ITO/CuI(40 nm)/active layer (60 nm)/Al (120 nm). This study clearly indicated that the devices made with CuI as an HTL showed superior performance than the device fabricated from PEDOT:PSS layer as an HTL. Morphological characterization of the HTL using scanning electron microscopy (SEM) and atomic force microscope (AFM) were carried for better understanding.

1. Introduction

Polymeric solar cells have been gained a significant attention in the last two decades due to their potential advantages like mechanical flexibility, simple fabrication processes, cost effective, light weight and large area fabrication process, which are essential for bulk scale production [1,2]. Till date the power conversion efficiency (PCE) and lifetime of the photovoltaic devices are not adequate for possible commercial applications. Many attempts have been projected to optimization of photovoltaic device to reach the highest possible PCE and lifetime of the device. Among them, introduction of active materials (donor and acceptor materials) and their optimization are the most studied [3–6]. In contrast, interfacial layer (hole transport layer; HTL and electron transport layer; ETL) have received scant attention for device fabrication, while interfacial materials are playing a vital role to improve the device performance. Especially, the HTL and their deposition method have significant importance for optimal device performance to reach the highest possible PCE.

Water soluble poly(3,4-ethylenedioxythiophene):poly (styrenesulfonate) (PEDOT:PSS) is the most successfully used HTL in organic solar cells because of its excellent transporting properties, high conductivity, optical transparency in the visible range and suitable work function. While several studies have been confirmed that due to its hygroscopic, protonation and acidic nature often corrode the ITO and affects the long-term stability of the photovoltaic devices [7–10]. On the other hand PSS free organic materials like small molecules based [11], graphene-based materials [12,13] and carbon nanotubes (CNTs) etc. are also used as HTL in organic solar cells, while the photovoltaic performances of these devices are not high as compared to PEDOT:PSS as an HTL. Transition metal oxides with a high work function, namely molybdenum oxide (MoO_x), vanadium oxide (V_2O_5), nickel oxide (NiO) and tungsten oxide (WO_3) so forth have been successfully used as HTL in organic solar cells to overcome the degradation issue of PEDOT:PSS [14–21]. It is worth to mention that thermal deposition of few metal oxides such as MoO_3 was worked even better as HTL compared to solution-processed deposition.

Recently, solution-processable deposition of metal oxides with a cost-effective method has been attracted significant for solar cells applications in general. Despite the significant efforts, however, there remains a clear need for the development of new, robust, inexpensive and solution-processable HTL for cost effective

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photovoltaic devices and in plastic optoelectronics more generally. Copper thiocyanate (CuSCN) was reported as an efficient solution-processable HTL in BHJ solar cells [22–24]. While, poor solubility of CuSCN has limits its applications as a solution-processable HTL for solar cells applications to the general public [22,24]. Recently, few reports have been appeared in literature for solution processed CuI as an HTL for polymeric solar cells [25–27]. Bian and co-workers demonstrated solution processable CuI as an HTL for poly(3-hexylthiophene):[6,6]-phenyl C_{61}-butyric acid methyl ester (P3HT:$PC_{61}BM$) [28] based polymeric solar cells and achieved to up to 4.15% PCE [25]. Alford and co-workers also reported P3HT:$PC_{61}BM$ based solar cells employing solution-processable CuI as an HTL and compared with PEDOT:PSS [26].

Solution-processable CuI as an HTL that have replaced PEDOT:PSS for device fabrication based on P3HT:$PC_{61}BM$ has been already reported [25,26]. Encouraged by the research of CuI over PEDOT:PSS as an HTL, we decided to explore the solution-processable CuI as an HTL for organic solar cells based on low band gap polymers for photovoltaic performances. In order to examine we have used PCDTBT [29] and PTB7 [30] as two low band gap donor materials blend with phenyl-C_{71}-butyric acid methyl ester ($PC_{71}BM$) as an acceptor material based on ITO/CuI/active layer/Al device configuration as shown in Fig. 1. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of PCDTBT, PTB7, $PC_{71}BM$ and CuI together with the work function of ITO, PEDOT:PSS and Al are presented in Fig. 2. The work function of CuI (−5.1 eV) is slightly higher lying compared to PEDOT:PSS (−5.2 eV), which may be suggested CuI is a better hole extraction layer. Moreover, the LUMO level of CuI is about 2.0 eV, which was higher lying than the LUMO of active materials (PCDTBT, PTB7 and $PC_{71}BM$) and as a result easily block the electron transport to anode electrode. Additionally, CuI is a hydrophobic in nature which may provide better compatibility with hydrophobic organic materials like PCDTBT and PTB7, which improve the ordering the organic materials and reduce the contact resistance between the active layer and interfacial layer. The chemical structures of the active materials of PCDTBT, PTB7 and $PC_{71}BM$ are presented in Fig. 3.

Here, we demonstrate that CuI as an efficient and solution-processable HTL for low band gap polymeric solar cells. Two different combinations of low band gap polymers (PCDTBT and PTB7) blended with $PC_{71}BM$ were used as an active layer for photovoltaic device fabrication. Referential devices based on PEDOT:PSS layer as HTL have been fabricated for PCDTBT and PTB7 respectively. In this present work, the resulted HTLs were

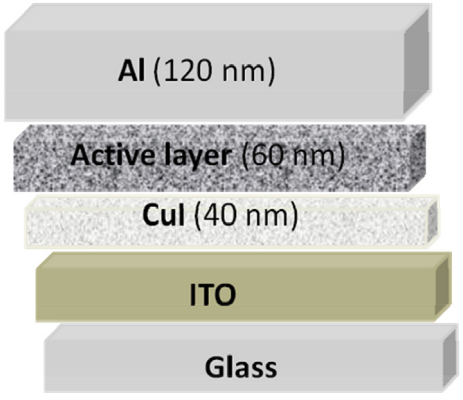

Fig. 1. Schematic diagram of the conventional polymeric solar cells in which the CuI layer is sandwiched between an ITO anode and active layer and the thickness.

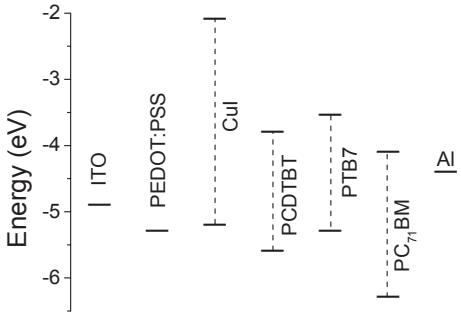

Fig. 2. Energy level diagram of the materials used in organic solar cells.

characterized by UV–vis–NIR spectroscopy, scanning electron microscope (SEM) and atomic force microscope (AFM) for better understanding to achieve the highest possible efficiency.

2. Experimental section

2.1. Materials

All chemicals and materials were purchased from Sigma–Aldrich, and Alfa-Aesar and used without further purification unless otherwise stated. PCDTBT, PTB7 and $PC_{71}BM$ were purchased from 1-material, Canada.

2.2. Preparation of CuI thin film as an HTL

10 mg of copper(I) iodide (CuI) was dissolved in 1.0 mL of acetonitrile and the resulting suspension mixture was sonicated for 1 h at room temperature. After sonication the mixture was kept for 10 min and the resulting clear solution was used for solution-processable HTL in organic solar cells.

2.3. Preparation of PEDOT:PSS as an HTL

Around 35 nm thickness PEDOT:PSS was deposited by spin casting. After that the resulting layer was annealed at 120 °C for 15 min. Then the active layer was deposited.

2.4. Preparation of active materials

PCDTBT:$PC_{71}BM$: The composition ratio of PCDTBT:$PC_{71}BM$ is1:4 that dissolved in a mixture of chlorobenzene and dichlorobenzene (1:3 ratio) in a concentration of 35 mg/mL.

PTB7:$PC_{71}BM$: The compositions ratio of PTB7:$PC_{71}BM$ is 1:1.5 that dissolved in a mixture of chlorobenzene and 1,8-diiodoctane (97:3 vol%) in a concentration of 25 mg/mL.

2.5. Device fabrication

The fabrication of polymeric solar cells was done on ITO coated glass slides based on ITO/HTL/active layer/Al. First, etching of ITO slides having a suitable pattern was done by using laser scribing system. Then the slides were cleaned using soap solution followed by several rinses with deionized water. The substrates were further cleaning in boiling acetone followed by trichloroethylene and isopropanol. After annealing the slides, a thin film of CuI (40 nm) layer was deposited by spin coating over it at 3500 rpm for 60 s (10 mg CuI in 1.0 mL acetronitrile). The resulting substrates were annealed at 100 °C for 15 min followed by dried at room temperature for 1 h. For reference devices 35 nm thickness of PEDOT:PSS as an HTL layer