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$CH_3NH_3PbI_3$ Perovskite Sensitized Solar Cells Using a D-A Copolymer as Hole Transport Material

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ABSTRACT

A conjugated D-A copolymer (P) having benzodithiophene donor and benzo[1,2,5]thiadiazole acceptor was employed as a p-type hole transporting material in solid state organic–inorganic hybrid solar cells and compared with the P3HT hole transporting material. In these device we have used organo-lead halide ($CH_3NH_3PbI_3$) synthesized by us, as light harvester. The power conversion efficiency (PCE) of 6.64% is achieved for the solar cell with P which is higher than that for P3HT (4.24%). The increase in PCE is mainly due to the enhancement in FF and V_{oc} and attributed to higher mobility of hole for conjugated copolymer than P3HT.

1. Introduction

Dye sensitized solar cells received considerable attention since the first report on 1991 by Grätzel and his coworkers, due to the excellent power conversion efficiency (PCE) of about 7% at a relatively low cost of fabrication [1] and are alternative to the conventional silicon based solar cells. A typical DSSC uses a monolayer of light absorbing sensitizer anchored on nanocrystalline TiO_2 to enhance light harvesting in a mesoporous environment in which charge separation also occurs at this surface. Lot of research has been carried out to enhance the PCE of these devices. As a result, PCE of 12.3% has been reported in 2011, by Grätzel research group for DSSCs based on an ortho-substituted porphyrin sensitizer, YD2-oC8, cosensitized with organic dye (Y123) with a cobalt electrolyte [2] which opened a new research area on porphyrin sensitized DSSCs [3]. However, the absorption spectrum of this porphyrin dye covers only the visible spectral region and lack of light harvesting ability beyond 700 nm limits the further enhancement in PCE for the DSSCs based on porphyrin dyes. Moreover, the long term stability of these devices might be an issue for future commercialization due to the use of volatile electrolytes. Various inorganic light absorbers with light harvesting capability that extends into the near infrared region were hence sought to replace these organic dyes.

Recent studies have reported that organometal halide perovskite mesoscopic solar cells with promising PCEs due to their excellent light harvesting and electron transporting properties and are perfectly suitable for use as prospective photovoltaic materials. In 2009, Miyasaka et al. reported the first perovskite ($CH_3NH_3PbBr_3$) sensitized TiO_2 solar cell using liquid electrolytes based on iodide and bromide and achieved a PCE of 3.1% under one sun illumination and 3.8% when $CH_3NH_3PbBr_3$ was replaced by $CH_3NH_3PbI_3$ [4]. Later on Park et al. [5] in 2011, reported improved PCE of 6.5% for modified TiO_2 solar cells sensitized with $CH_3NH_3PbI_3$ perovskite and an electrolyte based on iodide. They have used $Pb(NO_3)$ for modify the surface of mesoporous TiO_2 film before coating of perovskite film and acts as blocking layer in the solar cells. However, it was observed that the performance of devices based on perovskite materials and liquid electrolyte decreased by 80% in only few hours due to the instability of the perovskite material in the presence of liquid electrolyte due to the dissolution of perovskite. Hence it is essential to prepare perovskite based solar cells with a solvent free hole transport material (HTM) and called as solid state organic-inorganic hybrid solar cells. Park and coworkers [6] reported sub-micrometer thin film solid state solar cells attaining a PCE of 9.7% with a $CH_3NH_3PbI_3$ in mesoporous TiO_2 film. [7] Snaith and co-workers reported a similar perovskite, $CH_3NH_3PbI_3Cl$ that served as a light

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absorber for mesoscopic thin film solid state solar cells to attain a PCE of 10.9%, for which the mesoporous Al_2O_3 film served as scaffold to replace the n-type TiO_2 electron transporting layer. Recently, same group reported a significant enhanced PCE of 12.3% [8] for perovskite $CH_3NH_3PbI_{3-x}Cl_x$ solar cells, with the same device structure based on Al_2O_3. Soak et al. reported almost same PCE for solar cell based on another perovskite $CH_3NH_3Pb(I_{1-x}Br_x)_3$, with the mesoporous TiO_2 photoanode [9]. Recently, in 2013, Grätzel and co-workers, reported perovskite $CH_3NH_3PbI_3$ sensitized TiO_2 solar cells with a PCE approaching to 15% which set a new record for all solid state hybrid mesoscopic solar cells [10]. Therefore, this impressive PCE opened new channel for the development of third generation solar cells based on perovskite and HTM with the advantages of very high PCE, low cost, ease of processing and considerable durability [11] and efficiency approaching 20% is realistically possible from a solid-state mesoscopic solar cell based on $CH_3NH_3PbX_3$ (X = Cl, Br, or I) [12]. In all above perovskite solar cells, a HTM [2,2′,7,7′-tetrakis-(N,N-di-pmethoxyphenylamine) 9,9′-spiro-bifluorene] (spiro-OMeTAD) has been employed. However, conductivity of spiro-OMeTAD is low ($\sim 10^{-5}$ S/cm). Moreover, the spirobifluorene core in spiro-OMeTAD molecule is relative expensive due to extensive synthetic processes for preparation. So it would be important to develop a cheaper alternative of spiro-OMeTAD for commercial application of hybrid perovskite solar cells.

Alternative HTM materials with excellent electrical properties may be used in place of spiro-OMeTAD. Soluble donor-π-acceptor (D-π-A) can be the alternative choice as HTM. Conjugated polymers have been widely used in the field of polymer solar cells because of their easy processability, low cost and mechanical flexibility [13]. The solar cells using the combination of perovskite with mesoporous TiO_2 and P3HT as hole transport material, PCEs of 3.8%, 4.5% [14] and 6.7% [15] have been reported and recently a PCE of 10.8% have been achieved by Coning et al. for $CH_3NH_3PbI_2Cl$ perovskite [16].

To obtain high photovoltaic performance, it is importance that the HTM should show a good hole mobility and compatible highest occupied molecular orbital (HOMO) energy level to the semiconductor light absorber. Recently, Qiu have used a p-type low band gap conjugated D-A copolymer PCBTDPP as HTM and achieve an outstanding open circuit voltage of about 1.15 V for $CH_3NH_3PbBr_3$ sensitized hybrid solar cells and $CH_3NH_3PbI_3$ sensitized hybrid solar cell showed a PCE of 5.55% along with good stability [17]. Heo et al. have reported a ~12% [18] PCE in an organic-inorganic hybrid solar cell using a poly (triarylamine) (PTAA) HTM with an average PCE of 9.7% [19]. The D-A conjugated polymer P (chemical structure shown in Fig. 1) have the deeper HOMO level than P3HT and posses good stability than P3HT. Recently, Sharma et al. have used this copolymer as donor material for polymer solar cell along with PCBM and achieved a PCE of 3.45–5.30% [20]. These demonstrations indicate that the P can be used as HTM for hybrid solar cells.

In the present communication, we have used D-A conjugated copolymer P as HTM to investigate the solid state hybrid solar cells consisting of $CH_3NH_3PbI_3$ as the light harvester and mesoporous TiO_2 as photoanode. We have also fabricated the solar cells using P3HT as HTM for comparison. The inorganic-organic hybrid solar cell with P as hole transport material (PCE = 6.64%), showed higher PCE than that for P3HT (PCE = 4.24%) and attributed to the higher hole mobility of P as compared to P3HT. The enhancement in V_{oc} and FF for cell with P has been related to the deeper HOMO energy level of P and efficient hole transport, respectively.

2. Experimental details

Perovskite was synthesized following the reported procedure [6]. The P3HT was purchased from Aldrich and copolymer was synthesized as reported earlier [20].

2.1. Device fabrication and characterization

A 40 nm thick dense blocking layer of TiO_2 was deposited onto the pre-cleaned FTO substrate by spraying pyrolysis deposition carried out using a 20 mM titanium diisopropoxide bis(acetylacetone) solution (Aldrich) at 450 °C to prevent direct contact between FTO and HTM. The mesoporous TiO_2 films were coated from a TiO_2 paste (dye Sol 18NT-T paste diluted in anhydrous ethanol) by doctor blade technique. The films were dried at 80 °C for 1 min and then annealed at 450 °C for 30 min. The films were then treated in 40 mM of $TiCl_4$ aqueous solution at 60 °C for 1 hr and heat treatment at 450 °C for 30 min to improve the interfacial contact with nanocrystalline TiO_2. The perovskite $CH_3NH_3PbI_3$ solution was prepared as follow. The synthesized CH_3NH_3I powder was mixed with PbI_2 at a 1:1 mol ratio in dimethylformamide (DMF) and stirred over night at 60 °C, followed by filtering using a Whattman (0.45 μm) filter paper. The prepared solution of perovskite was dripped on the top of TiO_2 film and then spin cast at 2500 rpm for one minute. After that the perovskite sensitized TiO_2 film was placed on a top of hot plate at 100 °C for 45 min to form crystalline $CH_3NH_3PbI_3$. The heat treatment is essential for a complete conversion of precursor to final organo lead halide. The heated $CH_3NH_3PbI_3$ film exhibits better optical absorption and higher crystallinity [21]. We have used P3HT (commercially available and used without any further purification) and copolymer P. The polymer HTMs were spin coated on $CH_3NH_3PbI_3/TiO_2$/bl-TiO_2/FTO substrate at 2500 rpm for 30 s using HTMs solution in chlorobenzene and then dried for 1 hr. Finally a

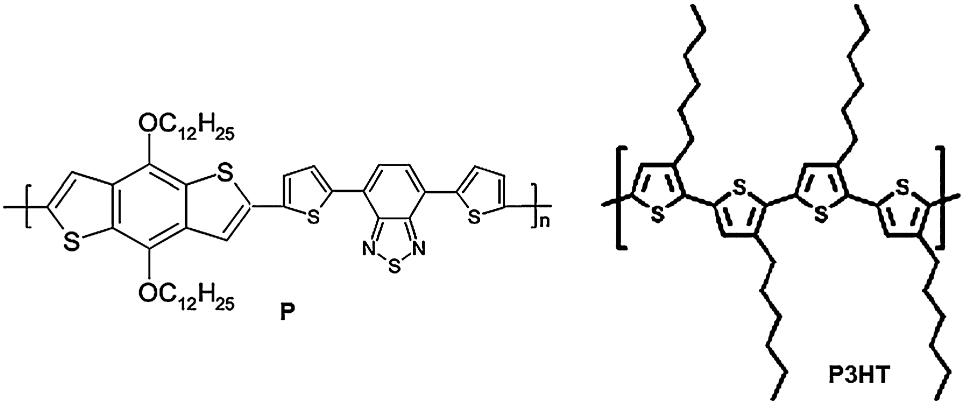

Fig. 1. Chemical structure of D-π-A conjugated copolymer P and P3HT.