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Interfacial modification of the electron collecting layer of low-temperature solution-processed organometallic halide photovoltaic cells using an amorphous perylenediimide

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ABSTRACT

The efficiency of organometallic halide photovoltaic cells can be improved by interfacial modification of the titanium oxide (TiO_x) electron collecting layer by a thin layer of an organic material. Enhancements of power conversion efficiency up to 37% were obtained with $PC_{61}BM$, but the performance is highly dependent on processing conditions and PCBM is still an expensive material. Herein, a glass-forming perylenetetracarboxylicdiimide derivative (PDI-glass) was used as interface material. The devices were optimized with varying PDI-glass thickness. With an optimal 10 nm-thickness, a power conversion efficiency increase of 39% were obtained, with an increase in short-circuit current from 9.7 to 11.05 mA cm^{-2} and fill factor from 0.51 to 0.61. Aside from the thickness of the PDI-glass layer, the process yields consistent results independent of the processing conditions. Photoluminescence spectra revealed the presence of charge transfer at the PDI-glass – active layer interface. The films were further studied by X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning electron microscopy (SEM).

1. Introduction

Significant progress has been achieved in solution-processed organic and hybrid thin film photovoltaic cells in the last few years, the driving forces of which is their potential low cost, light weight, flexibility, and simple fabrication methods [1]. Recently, photovoltaic cells based on organometallic halides, in particular methyl ammonium lead iodide ($CH_3NH_3PbI_3$), also known as perovskite, have received widespread interest in photovoltaic research. The low band gap (1.5 eV) [2], high charge carrier mobility ($8\,cm^2\,V^{-1}\,s^{-1}$) [3], high absorption coefficient ($1.5\times10^4\,cm^{-1}$), [2] low exciton binding energy (20 meV) [4] and long diffusion length (1 µm) [2], coupled with and easy and cost-effective synthetic route, makes perovskite an extremely appealing material for photovoltaic applications. Perovskite absorbs light strongly in the visible-near infrared region [5] and also acts as an electron and a hole transport material [6]. Several strategies such as synthesis of new materials, improvement of film quality by one-step and two-step processes, and interface control have been developed to improve the performance of perovskite PV cells for potential application [4]. To date, power conversion efficiencies over 19% have been reported in the literature [7]. However, most highly efficient perovskite PV cells reported so far use a condensed titanium dioxide electron transport layer that is processed at quite high temperatures (450 °C for 1 h) [8]. Unfortunately, organometallic halide PV cells with mesoporous titanium oxide processed at high temperatures may not be compatible with large-scale production on flexible substrates [2,5]. A TiO_x layer processed at low temperatures constitutes a promising alternative for flexible PV cells, because it can be processed at low temperatures, and is indefinitely stable, even when operated under aerobic conditions [9,10]. However, TiO_x yields lower efficiencies in comparison to compact mesoporous titanium dioxide. This lower performance is believed to be due to non-homogeneity and the presence of surface defects on the TiO_x layer that result in low quality of the photogeneration layer and low charge transport efficiency [11]. It

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is thus crucial to modify the surface of the electron-collecting TiO_x layer to improve charge collection. Recently, an approach involving low temperature, solution-processed planar-heterojunction organometallic halide PV cells have shown promise towards the development of highly efficient and flexible PV cells [2,5]. In planar heterojunctions (PHJ), the perovskite is sandwiched between an electron transport layer and a hole transport layer without requiring mesoporous titanium oxide. The benefits of this approach include a simple device fabrication and low-temperature processability. This approach was reported by Kim et al. in 2014 by modifying the surface of zinc oxide in planar heterojunction perovskite solar cells [4]. They reported a 30% enhancement of the efficiency of the devices after modification of the ZnO surface by a thin layer of $PC_{61}BM$. They observed that the incorporation of a thin layer of PCBM could modify the electronic structure of ZnO and reduce the traps/charge recombination at the ZnO/perovskite interface. Co-authors in this work also studied PCBM as modifier for TiO_x and the enhancement observed was 37% as published recently [12]. However, using PCBM as interfacial layer also resulted in other issues such as low coverage, interfacial recombination and leakage current [12]. Furthermore, PCBM offers limited potential to modulate the energy level by functionalization through synthesis, and is several orders of magnitude more expensive than perovskite.

Mexylaminotriazines are a class of glass-forming materials that usually show outstanding glass-forming ability with high kinetic stability towards crystallization. The glass transition temperatures (T_g) can be modulated by tuning their molecular structures [13]. Glassy mexylaminotriazine derivatives can contain functional groups that can be covalently bonded to chromophores, thereby resulting in adducts that can remain indefinitely in the amorphous state and can preserve the optical and electronic properties of the chromophores. This method was already implemented with a series of azobenzene dyes where glass-forming adducts were generated using a simple, efficient and high-yielding procedure [14], and with a series of 3,4,9,10-perylenetetracarboxylicdiimide (PDI) derivatives that could be incorporated into bulk heterojunction PV cells as electron acceptors in devices that gave performances comparable to crystalline PDI derivatives [15].

As compared to PCBM, perylenediimide derivatives are promising materials to modify the surface of the electron collecting layer because their optoelectronic properties can be easily tuned by tailoring the substituents on the imide groups or on the bay positions [16]. In addition, PDI chromophores strongly absorb light in the visible region, which may provide an additional contribution to the overall light harvesting of the device. In such process, the low-lying HOMO levels of PDI derivatives may facilitate the hole transfer process from the PDI molecules to the organometallic halide after light absorption [17]. The glass-forming properties of PDI-functionalized molecular glasses are also appealing because the amorphous nature of the resulting thin films is expected to prevent the formation of grain boundaries, improve the surface morphology of the perovskite layer by increasing the surface adhesion and ensure optimal coverage in the interface between the TiO_x and perovskite layers, leading to enhanced electron transfer.

Herein, we demonstrate the surface modification of an electron-collecting layer TiO_x by a thin layer of an amorphous 3,4,9,10-perylenetetracarboxylicdiimide-functionalized mexylaminotriazine derivative (thereafter referred to as PDI-glass) as an interfacial layer. With our optimized interfacial modification by PDI-glass, the devices showed the best performance with an optimal thickness of 10 nm. The power conversion efficiency of the device increases by 39% by incorporation of an ultrathin layer of PDI-glass with an increase in short-circuit current from 9.7 to 11.05 mA cm^{-2} and fill factor from 0.51 to 0.61 [14].

2. Experimental

2.1. Materials

Lead iodide (PbI_2) was purchased from Tokyo Chemical Industry (Tokyo, Japan), and titanium (IV) oxysulfate ($TiOSO_4$) was purchased from Sigma-Aldrich (St. Louis, MO). Hydrogen peroxide (H_2O_2), N,N-dimethylformamide (DMF), Methylamine solution (CH_3NH_2) and Hydroiodic acid (HI) were supplied by Kanto Chemical (Tokyo, Japan). PDI-glass was synthesized according to literature procedures [15]. Ultraviolet-visible (UV–Vis) absorption spectra of perovskite films were measured using an absorption spectrophotometer (U-3310, Hitachi). Scanning electron microscopy (SEM) analysis was performed using a scanning electron microscope (SU1510, Hitachi High-Tech) operated at 100 kV. Surface morphology was investigated by atomic force microscopy (AFM; SII SPI3800N) in tapping mode. X-ray diffraction (XRD) patterns of the prepared films were measured using an X-ray diffractometer (Smart Lab, Rigaku) with an X-ray tube (Cu Kα, λ=1.5406 Å).

2.2. Synthesis

2.2.1. Synthesis of methylammonium iodide

Methylammonium iodide (CH_3NH_3I) was synthesized by a modification of a procedure reported in the literature [6]. 55% Aqueous hydriodic acid (11.0 mL) was added dropwise with constant stirring to a mixture of methylamine solution (40 wt% in water, 7.75 g) and methanol (30 mL) in a 100 mL conical flask equipped with a magnetic stirrer. The reaction is exothermic and a cloudy fume is formed. The mixture was stirred continuously with a magnetic stirrer for one hour, at which point the resulting solution was dried under reduced pressure using a rotary evaporator. The yellow brown solid formed was dissolved with ultrasonication in anhydrous methanol, yielding an orange solution that was added gradually in a beaker containing 450 mL ethyl acetate with constant stirring. The resulting white precipitate was filtered by vacuum filtration and washed 2–3 times with ethyl acetate to remove unreacted starting materials. The resulting white solid was dried under vacuum for 6 h at 70 °C.

2.3. Device fabrication

Indium tin oxide (ITO) coated glass substrates with sheet resistance 10 Ω sq^{-1} were pre-treated with oxygen plasma for 20 min. An amorphous layer of TiO_x was deposited above the ITO-glass by low temperature chemical bath deposition (CBD) method, as reported in the literature [18]. A thickness of 60 nm was selected, because it was shown to yield optimal results in a previous study [19]. In this method, the electron-collecting layer TiO_x was deposited in an aqueous solution of titanium (IV) oxysulfate ($TiOSO_4$) and hydrogen peroxide (H_2O_2) for 16 min in an oil bath at 80 °C. An amorphous film was produced after heating to 150 °C for 1 h on a hot plate. PDI-glass films of different thicknesses (5–15 nm) were deposited onto the TiO_x by spin-coating from a PDI-glass solution (10 mg/mL) in chlorobenzene at different spinning speeds for 60 s. The PDI-glass film was dried at room temperature for 10 min. A 200 nm perovskite film was deposited above the TiO_x/PDI-glass layer by spin-coating from a perovskite ($CH_3NH_3PbI_3$) solution in DMF at 3000 rpm for 40 s. The films were allowed to dry at room temperature for 10 min and annealed at 100 °C for 10 min [20]. The hole transport layer was deposited by spin-coating of a 0.058 M solution of spiroOMeTAD containing 0.19 M 4-*tert*-butylpyridine, 0.031 M $LiNTf_2$ and 5.6×10^{-3} M Co(2-pyrazolyl-4-*tert*-butylpyridine)$_3(NTf_2)_3$ at 4000 rpm for 30 s. The films were allowed to evaporate for 10 min under N_2 in a glove box and annealed at 70 °C for 20 min. Finally, 100 nm of Au was deposited under high vacuum above