Interface engineering of compact-TiO$_x$ in planar perovskite solar cells using low-temperature processable high-mobility fullerene derivative

Md. Shahiduzzaman[a,b,*], Makoto Karakawa[b,c,d], Kohei Yamamoto[c], Takuji Kusumi[c], Kyosuke Yonezawa[c], Takayuki Kuwabara[c,d], Kohshin Takahashi[c,d], Tetsuya Taima[b,c,d]

[a] Department of Chemistry, Faculty of Science, Tokai University, Kanagawa 259-1292, Japan
[b] Institute for Frontier Science Initiative (InFiniti), Kanazawa University, Kanazawa 920-1192, Japan
[c] Graduate School of Natural Science and Technology, Kanazawa University, Kanazawa 920-1192, Japan
[d] Research Center for Sustainable Energy and Technology, Kanazawa University, Kanazawa 920-1192, Japan

ARTICLE INFO

ABSTRACT

Interface engineering plays a promising strategy to produce highly efficient planar heterojunction (PHJ) perovskite solar cells. The deep trap states on the compact-TiO$_x$ surface leading to a large leakage current and recombination of charge carriers. To solve the problems, interfacial engineering of electron collecting layer (ECL) compact-TiO$_x$ by a thin-layer of one-step solution-processed and low-cost organic material is applied. In contrast, commonly used PCBM is still expensive material. Herein, a new, low-temperature processable higher potential of [60]fulleropyrrolidine derivatives named as *N*-phenyl[60]fulleropyrrolidines (PNP) was introduced as an interfacial modification of ECL compact-TiO$_x$ with the varying thickness of 10, 20, and 30 nm to replace the commonly used PCBM in PHJ perovskite solar cells. The modified surface morphology was achieved by introducing PNP interfacial layers that enhanced the surface-energy properties of the cells in terms of enhanced photocurrent. Compared with PCBM, PNP features a higher electronic mobility and stronger hydrophobic nature. The enhancement of power conversion efficiency was obtained from 5.12% to 8.23%, with an increase in short-circuit current density (J_{sc}) from 11.90 to 21.44 mA cm^{-2} and fill factor (FF) from 0.49 to 0.56 owing to insertion of optimum 10-nm-thickness PNP that led to more efficient electron transport and charge extraction in the solar cell performances. The present work provides an important sign in the aspects to the low-cost mass production of perovskite solar cells.

1. Introduction

Hybrid organic-inorganic perovskites (e.g., CH$_3$NH$_3$PbI$_3$) have emerged as a promising photosensitive layer for the third-generation thin-film photovoltaics due to their potential low-cost and solution-processable with a tunable band gap and strong absorption coefficients [1]. The efficiency of perovskites with 3.8% power conversion efficiency (PCE) was first reported by Kojima et al. [2] The encouraging discovery has been continued further to achieve a notable PCE of 22.01% until the date [3]. High performance perovskite solar cells are mainly fabricated by two dominant device configurations named as mesoporous structured and planar heterojunction (PHJ) structured [4]. Apostolopoulou et al. [5] reported a composite mesoporous titanium dioxide (TiO$_2$)-In$_2$O$_3$ electron collection layers (ECL) as an efficient scaffold that significantly enhanced PCE up to 12.9% of perovskite solar cells. Enhanced performance of heterojunction solid state perovskite solar cells have been reported [6] by insertion of porous-TiO$_2$ between

compact-TiO$_2$ and perovskite. An approach involving a clean and flexible synthesis of TiO$_2$ nanocrystallites was used for dye-sensitized solar cell and perovskite solar cells, which notably improved performances with the PCE of 9.5% and 15.3%, respectively. Huang et al. [7] reported perovskite solar cells with a PCE of 15.08% using a room-temperature reactive magnetron sputtering method for the preparation of TiO$_2$ nanopillars layer. Besides, SrTiO$_3$ was introduced as an interfacial modification layer of mesoporous TiO$_2$ with varying concentration solution of Sr(NO$_3$)$_2$ in perovskite solar cells that remarkably enhanced PCE of 11.4% [8]. Gheno et al. [9] demonstrated that the printable WO$_3$ based perovskite solar cells have revealed the drastic improvement of device stability compared to that of TiO$_2$. This printable interfacial layer processed at low-temperature and showed an improvement of their photovoltaic parameters upon storage, as long as no UV light is involved. Li et al. [10] reported that PCE increased considerably from 12.4% to 17.2% upon the insertion of a lanthanum doped TiO$_2$ compact layers between FTO and perovskite layer. They

also revealed that lanthanum dopants facilitated to the improvement in photo-stability of perovskite solar cells. The preparation of high-quality mesostructured films and compact TiO_2 layers involves high-temperature processes (> 450 °C), which is too high up for commercial applications [11,12]. In the absence of mesoporous TiO_2 layer, several groups have circumvented the limitation by improving the performance of PHJ perovskite solar cells [13,14]. In particular, some low-temperature processed ECL materials such as TiO_2, ZnO, and SnO_2 are commonly used in organic and perovskite solar cells [4,15–17]. Besides, Wang et al. [18] reported a low-temperature-processed nanocomposite of pristine graphene nanoflakes and anatase-TiO_2 nanoparticels as ECL that significantly enhanced the photovoltaic performance of perovskite solar cells. Wu et al. [19] stated that the perovkite solar cells with a PCE of 14.0% were fabricated by using 5.0 mol% Zn-doped TiO_2 compact layer. In addition, low-temperature solution processed SiO_2-TiO_2 composite layer based-perovskite solar cells were fabricated with the PCE of 14.8%. This SiO_2-TiO_2 composite layer is facilitated to the better charge extraction and reduced surface recombination at the interface of FTO/perovskite compared to individual SnO_2 and sintered TiO_2 layer [20]. Recently, Ye *et al.* [21] reported compact-TiO_2 with varying annealing temperature-based $FA_{0.81}MA_{0.15}Pb(I_{0.836}Br_{0.15})_3$ perovskite solar cells were fabricated and the optimum devices exhibited with the PCE of 16.6% and good stability. Wu et al. [22] reported the perovskite solar cells with a PCE of 19.5% that was fabricated by TiO_2 nanowire. Furthermore, Gan et al. [23] exhibited the PCE of perovskite solar cells based on PHJ $(PEA)_2(MA)_2Pb3I_{10}$ up to 3.7% by optimizing the TiO_2 nano-rod with 600 nm-long as scaffolds. Besides, perovskite solar cells with pintable carbon counter electrode were fabricated with a PCE of 7.5% by using mesoscopic TiO_2 nanosheets and NiO nanosheets as ECL and hole transport layer (HTM), respectively [24]. Jung et al. [25] reported inorganic $RbPbI_3$ perovskite solar cells that facilitated the superior stability in environmental conditions. Kuwabara et al. [26] reported low-temperature, -cost, simple and scalable chemical bath deposition (CBD) technique that allowed a uniform, compact, and air-stable amorphous compact-TiO_x film, and used as a ECL layer for efficient organic photovoltaic (OPV) and perovskite solar cells [27].

However, low-temperature processed TiO_2 used as a ECL material led the following drawbacks in PHJ perovskite solar cells. (i) the low electron mobility that led to charge accumulation in the TiO_2 layer [28,29]. (ii) Exposure of TiO_2 to UV light further induces formation of oxygen vacancies that are energetically deep trap levels responsible for severe recombination loss [30,31]. As a result, the interface of TiO_2/perovskite retards the photo-response of the resulting devices, leading strong hysteresis behaviors, and consequently making accurate efficiency measurement difficult [29]. Snaith et al. reported highly stable perovskite solar cells by inert metal oxides (Al_2O_3 etc.) to replace commonly used TiO_2 [30]. Another efficient way to avoid this challenge reported to alter the TiO_2 surface using a self-assembled monolayer (SAM) of fullerene derivatives [32,33]. In our previous work, we reported that the interface engineering morphology can play a major role in tuning the surface energy and enhanced the performance of PHJ perovskite solar cells with the PCE of 9.5% [34]. Recently, Co-authors reported that the PDI-glass to replace PCBM as modifier for TiO_x and enhancement observed was 39% [35]. Taking these concerns into consideration, it is urgent to explore the high-throughput manufacturing technique, low-cost and -temperature processing efficient electron transport material to replace high-cost PCBM or highly purified C_{60} is essential for efficient PHJ perovskite solar cells in order to obtain efficient electron collection and hole blocking. A high potential of [60] fulleropyrrolidine derivatives, which are promising alternative to PCBM for organic solar cells under Prato reaction conditions, have been reported the utility of inexpensive, simple and scalable one-step synthetic procedure [36]. Therefore, considering low-cost device fabrication, we used the higher potential of 2-phenyl[60]fulleropyrrolidines (PNP) as an interfacial modification of compact-TiO_x to replace PCBM in planar perovskite solar cells.

In this study, we demonstrate the surface modification of an ECL compact-TiO_x by introducing PNP as an interfacial layer in PHJ perovskite solar cells and investigate the effect upon the thickness of the PNP layer on the resulting device performances. To have desirable electrical properties, we chose PNP material due to higher electron mobility for efficient transfer [37]. PCE is improved by tuning surface energy through optimization of morphology in terms of enhanced photocurrent. Compared with PCBM, the formation of a chemical bond between compact-TiO_x and PNP, as well as the low-solubility of PNP in *N*, *N*-dimethylformamide (DMF), make PNP layer more stable, most of which cannot be washed away during the fabrication of the perovskite layer. The PNP interfacial layer can also act as the hole blocking layer that reduce the hole recombination at the compact-TiOx/PNP interface and enhanced the electron extraction by the ETL.

2. Experimental section

2.1. Materials

Lead iodide (PbI_2, purity 98%) and methylammonium iodide (CH_3NH_3I, purity 98%) was purchased from Tokyo Chemical Industry (Tokyo, Japan), while titanium (IV) oxysulfate ($TiOSO_4$, purity 99.99) were from Sigma Aldrich (St. Louis, MO, USA). Hydrogen peroxide (H_2O_2, purity 35%) and *N, N*-dimethylformamide (DMF, purity 99.5%) were supplied by Kanto Chemical (Tokyo, Japan). The PNP was synthesized under simple prato reaction conditions according to the procedure described by Karakawa *et al.* [36] The scanning electron microscopy (SEM; SU1510, Hitachi High-Tech, Tokyo, Japan) together with atomic force microscopy (AFM; SII SPI3800N, Seiko, Japan) were used to analyze the surface morphology. Ultraviolet-visible (UV–Vis) absorption spectra of perovskite films were measured by an absorption spectrophotometer (U-3310, Hitachi, Tokyo, Japan). The X-ray diffraction (XRD) patterns of the prepared films were measured using an X-ray diffractometer (SmartLab, Rigaku, Japan) with an X-ray tube (Cu Kα radiation, $\lambda = 1.5406$ Å). (Surf.corder; ET 200, Tokyo, Japan) was used to measure the thickness of the films.

3. Device fabrication

Indium tin oxide (ITO)-patterned glass substrates with sheet resistance 10 Ω sq^{-1} were pre-treated in oxygen plasma for 20 min prior to use. An amorphous layer of compact-TiO_x films was deposited on the ITO-glass by low-temperature chemical bath deposition (CBD) method according to the procedure described by Kuwabara et al. [26] The PNP layers of different thicknesses 10, 20, and 30 nm were deposited onto the TiOx by simple spin-coating from a PNP solution (10 mg/mL) in chlorobenzene. (PbI_2; 0.144 g) and (CH_3NH_3I; 0.05 g) were dissolved in DMF; 615 μL with a molar ratio of 1:1 by shaking (VMR-5R, As-One) at room temperature (RT) for 30 min to produce a clear 25 wt% perovskite solutions. A 200-nm perovskite thin-film was deposited onto the TiOx/PNP layer by spin cast. The thin-films were then allowed to anneal at 100 °C for 10 min in a glove box under an inert environment. The hole-transporting layer consisting of 2,2′,7,7′-tetrakis (*N,N*-di-p-methoxyphenylamine) $- 9,9′$-spirobifluorene (spiroOMeTAD) in chlorobenzene (0.058 M) containing 4-*tert*-butylpyridine (0.19 M), lithium bis(trifluoromethylsulfonyl)imide (0.031 M), and tris[2-(1H-pyrazol-1-yl)-4-*tert*-butylpyridine]cobalt(III) tris[bis(trifluoromethylsulfonyl) imide] (5.6×10^{-3} M) as dopants was deposited by spin coating at 4000 rpm [38,39]. The resulting thin-films were annealed at 70 °C for 20 min on a hot plate in the glove box. After that, the thin-films were transferred in a vacuum chamber and 100-nm-thick silver (Ag) electrodes were deposited on the spiroOMeTAD layer at 2.22×10^{-4} Pa. The area of the devices is 0.04 cm^{-2}.