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High performance perovskite solar cells with functional highly porous TiO₂ thin films constructed in ambient air

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ABSTRACT

In the present work we report the synthesis of highly meso- and macro-porous thin TiO₂ films as efficient scaffolds for improved performance of heterojunction solid state perovskite solar cells made in ambient air. TiO₂ films were prepared using sol-gel process and Pluronic P-123 block copolymer as organic template while they were formed on conductive glass substrates by spin-coating method. The films were employed to the construction of very efficient perovskite solar cells made at ambient conditions where CH₃NH₃PbI_{3-x}Cl_x mixed halide perovskite was used as light harvester and P3HT polymer as hole conductor. The very rough and highly porous TiO₂ films proved to be an excellent host material for perovskite growth. The structural properties of the TiO₂ electron transport layer, thickness, particle size and porosity, strongly affected the overall conversion efficiency. The optimal structure and materials composition exhibited a notably high current density J_{sc} of 23.8 mA/cm², V_{oc} of 0.995 V and fill factor of 0.58. These solar cells prepared under ambient conditions yielded an average power conversion efficiency of 13.7% among the best ever recorded with P3HT polymer as hole conducting material.

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1. Introduction

Almost twenty five years ago, dye-sensitized photoelectrochemical solar cells (DSCs) which belong to the third generation photovoltaics, were originally proposed as an alternative technology with competitive performance to amorphous silicon based photovoltaic cells [1–4]. The main advantages over the conventional photovoltaics were among others the simple fabrication process, transparency, and relatively low cost [5,6]. Moreover, new and smart applications employing DSCs appear every year since the first demonstration of this technology. However, the moderate efficiency and the presence of liquid electrolytes put serious obstacles to the commercialization of DSCs. In particular, the 13% overall performance but in extra small devices [7] in combination with the several problems, which arise with dye's decoloration under UV light [8] and electrolyte leakage [9] may not guarantee the success of this technology in transferring to the production line. Indeed, the use of liquid electrolytes for high performance solar cells causes several problems to the fabrication steps because of leakage and volatilization issues of

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solvents in combination with poor long term stability of liquid based electrolytes. On the other hand, DSCs using hole transporting materials instead of liquid electrolytes exhibited much lower overall performance and finally serious barriers to their commercialization [10,11]. Fortunately in very recent years, organometal halide perovskite, CH₃NH₃PbX₃, where X is a halogen atom (I, Cl, Br, or a combination of some of them) with polycrystalline structure, has been proposed as an alternative light harvesting material for photovoltaic applications with promising results and obvious improvements to the third generation solid state photovoltaic cells [12–16]. Organometal halide perovskite materials are direct bandgap semiconductors with an approximately ideal bandgap for solar radiation on the surface of the earth of around 1.55 eV and high absorption extinction coefficient [17]. The overall conversion efficiency of these cells has been increased from 4% to almost 20% in only five years from their first demonstration [18]. Indeed, these organohalide perovskites exhibit very high efficiency mainly due to the excellent optical properties, ambipolar charge transport and finally the very long and balanced electron-hole diffusion lengths [19]. The most common so far implemented structure of a perovskite solar cell (PSC) is: transparent conducting oxide (TCO)/very thin compact TiO₂ layer/a few hundred nanometer thick TiO₂ or alumina mesoporous scaffold/perovskite/hole transporting layer (HTL)/evaporated metal [20]. Devices based on mesoporous TiO₂ are generally fabricated on

fluorine-doped tin oxide substrates (FTO) and a high annealing temperature (up to 500 °C) is necessary to form a well-connected nanostructure path for electrons' transport [21]. Although perovskite devices with a planar structure based on compact TiO₂ layer and poly(3-hexylthiophene) (P3HT) as HTL material yielded an overall performance over 10%, there is much space for further improvement [22]. Sarkar et al. reported the formation of a well-organized mesoporous TiO₂ using a block copolymer to achieve a maximum efficiency of 12.8% [23]. In general, mesostructured solar cells with porous TiO₂ are of great interest because of the variety of TiO₂ morphologies and structure control can be achieved in the presence of organic templates while the remarkable particle interconnection may guarantee enhanced charge mobilities [24–26]. Although other oxides as electron collection materials are also applied, TiO₂ is still the material of choice for high efficiency PSCs. However, the key factor towards high efficiency is the control and growth conditions of the materials but mostly the control of the interface between the perovskite and the TiO₂ nanoparticles [27,28]. Another important issue is the employment of spiro-MeOTAD as HTL. Recently, Ahn et al. reported an impressive 19.7% PCE incorporating a mesoporous TiO₂ network and spiro-MeOTAD as HTL by solution engineering method with excellent reproducibility [29]. Concern has been expressed as to the cost and the stability of this material, therefore, efforts have been made to introduce alternative molecular HTLs [30]. In this respect, P3HT is a standard hole transporter, which has been repeatedly used in several types of organic and hybrid solid state solar cells, with acknowledged functionality and stability.

Herein, we report the employment of highly porous TiO₂ films as a functional component of perovskite solar cells with very promising results. The proposed structure is very simple and straightforward with small structural risks: FTO/compact-TiO₂/porous-TiO₂/CH₃NH₃PbI_{3-x}Cl_x/P3HT/Au. In particular, nanocrystalline TiO₂ films were synthesized by using Pluronic P-123, ethylene oxide (EO), and propylene oxide (PO) block-copolymer as organic template for highly porous films, which finally proved that the growth of perovskite on these TiO₂ films created efficient pathways for electrons. In this respect, the present results emphasize the importance of the geometry of the materials interface for high performance solar cells which may also open new directions for PSC technology.

2. Experimental details

2.1. Materials

Titanium diisopropoxide bis(acetylacetonate) (75 wt% in isopropanol, Aldrich), Titanium(IV) butoxide (97%, Aldrich), anhydrous dimethylformamide (DMF), chlorobenzene, Pluronic P123 (5.800 g/mol, Aldrich), regioregular poly(3-hexylthiophene-2,5-diyl) (P3HT, 95.5%, 94.000 g/mol, Ossila), Lithium Bis(trifluoromethane)sulfonimide (Li-TFSI, 99.95%, Aldrich), 4-tert butylpyridine (4-TBP, 96% Aldrich), and all solvents were used as received.

2.2. Solar cell fabrication and materials characterization

Perovskite solar cells were fabricated under ambient conditions. Ambient humidity was higher than 35%. Solar cells were fabricated on fluorine-doped tin oxide glass substrates with a sheet resistance of 8 Ω/square (Pilkington). FTO substrate was patterned by chemical etching with Zinc powder and HCl aqueous solution. The conductive substrates were cleaned with detergent solution and acetone in ultrasonic bath and dried under nitrogen flow. A thin dense compact TiO₂ layer (c-TiO₂) was deposited on the etched FTO substrate by spin coating (2000 rpm, 10 s) using a titanium diisopropoxide bis(acetylacetonate) solution in isopropanol at a volumetric ratio of 1:9 followed by calcination at 500 °C for 15 min. Porous TiO₂ films (TiO₂-

P123) were prepared from a solution containing 0.23 M Titanium(IV) butoxide, 0.4 ml acetic acid, and 0.3–0.7 g Pluronic P123 block-copolymer in 4 ml isopropanol. Porous TiO₂ were directly deposited on top of the c-TiO₂ by spin coating at 1200 rpm for 20 s and dried for 10 min at 120 °C and 30 min at 500 °C. This step was repeated multiple times until optimal thickness was observed. Finally, highly ordered and porous TiO₂ films were formed. The porous nanostructure was examined for comparison against the commonly used commercial TiO₂ paste (P25, Degussa). In particular, TiO₂ paste was prepared by mixing nanocrystalline titanium dioxide, terpineol, ethyl cellulose in ethanol solution (TiO₂-P25), and spin coated at 3000 rpm for 30 s. Methylammonium iodide (CH₃NH₃I) was synthesized by reacting 12 ml methylamine (33% in ethanol), 5 ml HI (57% in water, Aldrich), and 20 ml ethanol in a 50 ml round-bottomed flask at 0 °C for 2 h. The crystallization of methylammonium iodide was achieved after carefully evaporating the remaining water and ethanol and a white powder was formed. Recrystallization of CH₃NH₃I occurred after several washes with anhydrous diethyl ether. 40 wt% precursor perovskite solution resulted after methylammonium iodide and lead (II) chloride were dissolved in anhydrous DMF in a molar ratio 3:1. The perovskite solution was then deposited onto TiO₂ electrodes by spin coating at 2000–4000 rpm for 45 s, followed by drying on a hot plate at 100 °C for 30 min under ambient conditions. A regioregular poly-3-hexylthiophene (94.000 g/mol) was dissolved in chlorobenzene (15 mg/ml), containing 25 mM Lithium bis(trifluoromethanesulfonyl) imide and 76 mM 4-TBP. P3HT was then deposited by spin-coating at 1200 rpm for 10 s, a procedure that was repeated twice in some cases to obtain a thicker hole conductor film. Thicker hydrophobic P3HT films found to protect perovskite from humidity as well as providing much more effective charge collection ability. Then solar cells were dried for 5 min at 60 °C to completely evaporate chlorobenzene. After HTM deposition samples were deposited into a high vacuum chamber (10⁻⁶ Torr) in order to complete cells with non-corrosive gold back contacts in a relative thickness of 100 nm. The active area of the solar cells was limited to 0.069 cm² using a mask. UV–vis absorption measurements were carried out using a Shimadzu UV-2600 spectrophotometer with an integrating sphere. Steady state photoluminescence spectra of perovskite solar cells were measured with Hitachi F2500 fluorescence spectrophotometer using an optional detector to extend measurement range up to 850 nm. Films were irradiated with 528 nm excitation wavelength, under room temperature. Structural properties of the films, pore size distribution, and BET surface area were measured with a Micromeritics Tristar 3000 analyzer equipped with a SmartPrep degasser. TiO₂ samples were firstly deposited onto glass substrates, calcined at 500 °C, and then scratched from films to obtain powders. Samples were degassed for 1 h under N₂ flux at 300 °C before measurement. Current–voltage curves were measured by a solar simulator Solar Light (16S-300) equipped with a Xenon lamp (measured at 100 mW/cm² with a Newport power meter, Model 843-R) and a Keithley 2601 A source meter. We need to mention a detail concerning measurements conditions and more specifically to the time delay applied among the data points in *J*–*V* characteristic curves. 50–100 ms delay could give the same *J*–*V* curve but an open circuit voltage drop (100 mV) was recorded in the case that a 150–200 ms delay was put to the measuring instrument. Therefore, delay of 50 ms among data collection was prior set to all measurements. Film's morphology was determined using a Field Emission Scanning Electron Microscopy (FE-SEM, Zeiss Supra 35VP). IPCE values were obtained with an Oriel IQE 200 system. X-ray diffraction measurements were made using a Bruker diffractometer (D8 Advance) with CuKα ($\lambda = 1.5406 \text{ \AA}$) radiation and Bragg–Brentano geometry was employed for X-ray diffraction studies.

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