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Efficient polymer:fullerene bulk heterojunction solar cells with n-type doped titanium oxide as an electron transport layer

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ABSTRACT

We have reported a highly n-type doped solution-processed titanium metal oxide (TiO_x) for use as an efficient electron-transport layer (ETL) in polymer:fullerene bulk heterojunction (BHJ) solar cells. When the metal ions (Ti) in TiO_x are partially substituted by niobium (Nb), the charge carrier density increased, by an order of magnitude, because of the large electronegativity of Nb compared to that of Ti. Therefore, the work function (WF) of Nb-doped metal oxide (Nb-TiO_x) decreases from 4.75 eV (TiO_x) to 4.66 eV (Nb-TiO_x), leading to an enhancement in the power conversion efficiency (PCE) of BHJ solar cells with a Nb-TiO_x ETL (from 7.99% to 8.40%).

1. Introduction

Bulk heterojunction (BHJ) solar cells composed of π-conjugated polymers (π-CPs) and fullerenes have attracted considerable attention as a promising energy source because of their low cost, solution processability, and large area obtained using roll-to-roll fabrication [1,2]. Over the past decades, many efforts have been devoted to increasing the power conversion efficiency (PCE) of BHJ solar cells for commercial applications [3–5]. Consequently, PCE of greater than 10% in BHJ solar cells has recently been reported, indicating a promising outlook for the commercialization of BHJ solar cells in the near future [4,5]. However, despite these impressive advancements, further improvement of the PCE is still required. In general, PSCs use a structure of transparent bottom electrode-BHJ layer-top cathode. Because of incompatibilities at the interface of the active layer and electrodes, such as large contact resistance and energy level mismatching between two layers, BHJ solar cells frequently suffer an inefficient charge extraction from the active layer to electrodes [6,7]. Therefore, one of the approaching ways to improve the PCE of BHJ solar cells is to introduce an electron transport layer (ETL) between the BHJ layer and the electrodes [8,9]. Interface engineering by introducing the efficient ETL that can reduce charge recombination at the interface and align the Fermi energy level between the BHJ layer and the electrodes, plays a critical role in improving the PCEs of BHJ solar cells.

During the past decades, numerous ETL materials based on transition metal oxides (TMOs) for efficient PSCs have been developed such as titanium dioxides (TiO_2), titanium sub-oxides (TiO_x), and zinc oxide (ZnO), and other transition metal oxide nanoparticles [9,10], because of adjustable electronic structure of TMOs for aligning of the Fermi energy level between the BHJ layer and electrodes by developing doped TMOs [11]. For example, by introducing dopant materials such as niobium (Nb) metal ions into TiO_2, Ti metal ions can be substituted, altering the electronic structure of TiO_2. Thus, the doped TiO_2 exhibits n-type nature with increased charge carrier density and the reduced work function (WF) values [11]. Furthermore, because Nb, which is a group-V dopant for TiO_2, has a higher number of valence electrons and similar ionic sizes compared to Ti [12,13], the original crystalline structure of TiO_2 can be preserved and similar optical properties were observed in Nb-doped TiO_2 [14,15]. However, crystalline TiO_2 layers should be prepared at high temperature above 450 °C or by complex synthetic steps [12,16]. Furthermore, to synthesize the doped TiO_2 system, it is also required the harsh process such as sintering process [16–19], complex purifications, and long reaction time for 20 h [19]. Because such difficulties in the utilizing TiO_2 are incompatible with PSCs, which are fabricated by solution process with low-temperature, it is required to develop a low-temperature and solution-processable titanium oxide.

Sol–gel processed amorphous TiO_x is one of the promising ETLs for PSCs because of its excellent air-stability, charge transport, charge selectivity, and good wettability on organic layers [9,20]. In addition, sol–gel processed TiO_x can be synthesized using a simple synthetic method under low-temperature processing in a short reaction time. However, since the oxygen deficiency related doping of TiO_x is

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uncontrollable under the ambient air, other reliable doping process of the TiO_x should be required for efficient ETL. Therefore, in this work, we developed hetero metal atom doped metal titanium oxide, Nb-doped TiO_x, by introducing Nb ion as dopant in sol–gel synthesis of TiO_x with easy and low-temperature process. The resulting Nb-doped TiO_x showed the improved n-type characters compared with TiO_x: the reduced WF value and the increased charge carrier density. The Nb-TiO_x ETL improves the electrical contact between BHJ layer and metal cathode by reducing the charge recombination in the BHJ layer and facilitating charge extraction from BHJ layer to the metal cathode. Therefore, PSC with Nb-TiO_x ETL exhibited better device performance than device with pristine TiO_x ETL.

2. Experimental details

2.1. Materials

TiO_x was synthesized using a sol–gel procedure with titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$, Aldrich, 99.999%, 2 mL), 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.9 + %, 10 mL) and ethanolamine ($H_2NCH_2CH_2OH$, Aldrich, 99 + %, 1 mL). All materials were mixed for 5 min at RT. After this step, the precursor was refluxed for 1 h at 120 °C to remove the solvent. All procedures were performed under a N_2 atmosphere.

Nb-doped TiO_x was synthesized using a sol–gel procedure with titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$, Aldrich, 99.999%, 2 mL), niobium ethoxide ($Nb[OCH_2CH_3]_5$, Alfa Aesar, 99.999%, 22 mg), 2-methoxyethanol ($CH_3OCH_2CH_2OH$, Aldrich, 99.9 + %, 10 mL) and ethanolamine ($H_2NCH_2CH_2OH$, Aldrich, 99 + %, 1 mL). To synthesize Nb-TiO_x, niobium ethoxide was mixed with titanium (IV) isopropoxide with a 1 mol.% ratio of Nb to Ti. All materials were mixed for 5 min at RT. After this step, the precursor was refluxed for 1 h at 120 °C to remove the solvent. All procedures were performed under a N_2 atmosphere. The synthesized TiO_x and Nb-TiO_x precursor solutions were diluted with methanol (1:200 by weight). The chemical structures of TiO_x and Nb-TiO_x are presented in Fig. 1a.

2.2. Device fabrication

BHJ solar cells were fabricated on a pre-cleaned indium tin oxide (ITO)/glass substrate. An aqueous solution of poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate), PEDOT:PSS(VPAI 4083, H. C. Stark), was spin coated as a hole-transport layer (HTL). The ITO/PEDOT:PSS substrates were dried for 10 min at 150 °C in air and then transferred into a glove-box to spin-cast the active layer. A mixture of poly(thieno[3,4-b]thiophene-alt-benzodithiophene) derivative (PTB7-Th) and a fullerene derivative, [6,6]-phenyl-C_{71}-butyric acid methyl ester ($PC_{70}BM$) as an acceptor (1:1.5 by weight) in chlorobenzene solvent with diiodooctane (DIO) additive (3 vol.%) was spin-cast on top of the PEDOT layer. PTB7-Th and $PC_{70}BM$ were purchased from 1-Materials, Inc. and Nano-C, Inc., respectively. Then, a diluted precursor solution of TiO_x or Nb-TiO_x was spin-cast in air on top of the active layer. Next, the device was pumped down to vacuum (10^{-7} Torr), and a ~100 nm thick Al electrode was deposited. The device structure and the chemical structures of PTB7-Th and $PC_{70}BM$ are illustrated in Fig. 1b.

2.3. Measurements

Current density–voltage (*J*–*V*) curves were measured using a Keithley 237 source meter under Air Mass 1.5 Global (AM 1.5 G) irradiation from a calibrated solar simulator with an irradiation intensity of 100 mW/cm^2. The capacitance–voltage (*C*–*V*) measurement was performed using a semiconductor parameter analyzer (HP4284A) and LCR meter. The WF values of TiO_x and Nb-TiO_x films were measured using a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co. Ltd) under atmospheric conditions.

3. Results and discussion

3.1. Properties of Nb-doped TiO_x films

Fig. 2a presents the UV–Vis absorption spectra of the TiO_x and Nb-doped TiO_x films. Because we added 1 mol.% Nb to TiO_x, the absorption

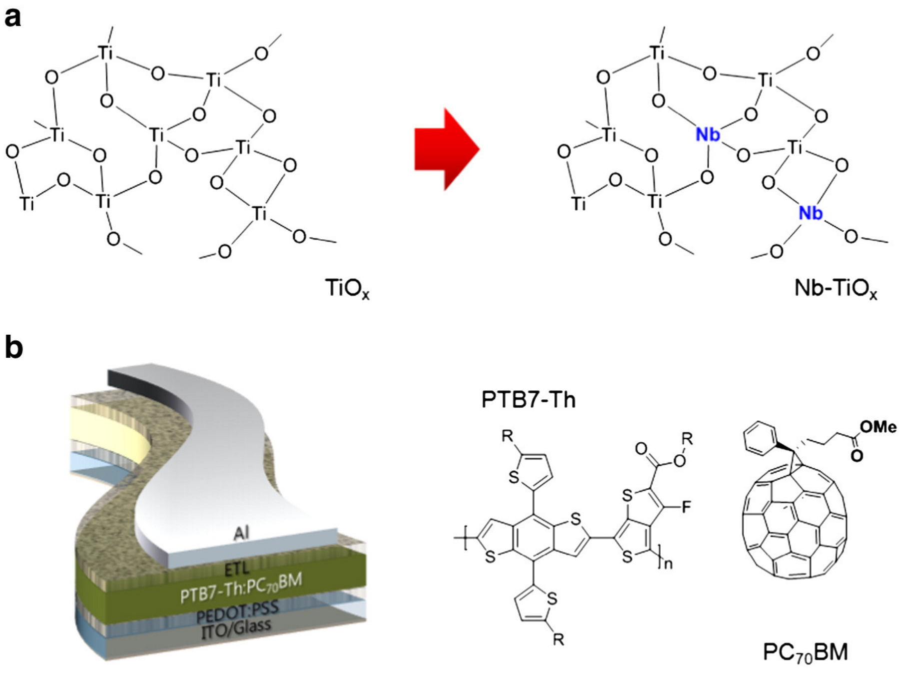

Fig. 1. (a) The chemical structures of TiO_x and Nb-TiO_x. (b) The device structure of PTB7-Th:$PC_{70}BM$ BHJ solar cells and the chemical structures of PTB7-Th and $PC_{70}BM$.