

Influence of p-type Doping to Dithiophene-Benzene Copolymer as Hole Transporting Layers in Perovskite Solar Cells

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Abstract

We fabricated perovskite solar cells (PSCs) employing dithiophene-benzene (DTB) copolymer as hole transporting material (HTM) without and with dopant, and then we measured current density-voltage characteristics of PSC devices. DTB is one of the promising materials for low cost and long term stability.

Device fabrication was performed under nitrogen atmosphere. After exposure to air for 5 hours, device performance was extremely bad, and the power conversion efficiency (PCE) showed 2.98%. However, device performance gradually improved by keeping in dry air. Finally, PCE reached 16.15% at 173 hours later.

When tris(pentafluorophenyl)borane (BCF) was added to DTB, initial characteristics improved and the PCE showed 13-14%. In addition, the PCE improved to 15-16% by keeping in dry air.

1. Introduction

For the past decade, perovskite solar cells (PSCs), which included power conversion layers of organic-inorganic halide perovskite structure, were actively investigated [1-3]. Spiro-OMeTAD was widely employed as hole transporting material (HTM) of PSCs. Generally, Li-TFSI was added as dopant due to its low charge mobility of spiro-OMeTAD. Recently, alternative materials have been explored because spiro-OMeTAD was expensive. Dithiophene-benzene (DTB) copolymer have been reported higher short circuit current density (J_{sc}) than other polymer semiconductors [4]. In addition, it was expected that DTB was low cost and high stability. However, the influence of oxygen and dopant have not been examined in detail yet.

In this research, we fabricated mesoporous-type PSC devices employing DTB copolymer as hole transporting layers (HTLs) under nitrogen atmosphere. Then, we examined the time dependence of current density-voltage (J - V) characteristics and the doping effect of a lewis acid tris(pentafluorophenyl)borane (BCF) [5-6].

2. Experimental Section

The structure of PSC devices was shown in Figure 1. First, c-TiO₂ layers were formed by spray pyrolysis method on glass substrates with fluorine-doping tin oxide (FTO) layers. After that, m-TiO₂ layers were formed by spin coating of TiO₂

particles-dispersed solution, and then by baking at 450°C. Next, perovskite layers were formed by the anti solvent method. Precursor solution, which dissolved CsI, formamidine hydroiodide (FAI), methylamine hydrobromide (MABr), PbI₂, and PbBr₂ in mixed solvent of N,N-Dimethylformamide (DMF) and dimethyl sulfoxide (DMSO), was adjusted the composition to Cs_{0.05}FA_{0.79}MA_{0.16}PbI_{2.52}Br_{0.48}.

We synthesized DTB copolymer as shown in Figure 2(a). HTLs were formed by spin coating of the dissolved DTB in chlorobenzene (thickness: about 20 nm). BCF (Figure 2(b)) was added to the DTB solution as necessary. Finally, Au electrodes were formed by the vacuum evaporation.

J - V measurements of the devices under solar simulator illumination (AM1.5G) were performed in air. Device samples were kept in the desiccator, which was controlled humidity under 5%RH. During the measurements, samples were taken out in air.

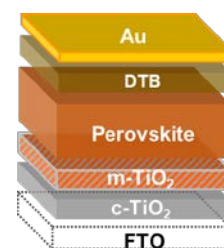


Fig.1 The structure of PSC devices.

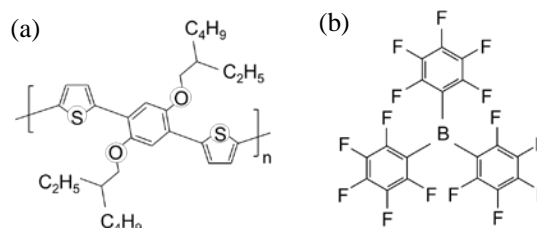


Fig.2 Molecular structure of DTB(a) and BCF(b).

3. Results and Discussion

Firstly, we fabricated PSC devices employing DTB copolymer without dopant, and then we examined the time dependence of device performance. Typical J - V characteristics were shown in Figure 3. After exposure to air for 5 hours, the power conversion efficiency (PCE) showed 2.98%, and series resistance (R_s) showed relatively high value of 32.02 Ωcm^2 . Later, R_s decreased to 3.708 Ωcm^2 after keeping in dry air for 173 hours, and PCE increased up to maximum value of 16.15%. PCE maintained the value of over 90% after 4 weeks.

BCF : None / Solvnt Concentration : 7.50 mg/mL

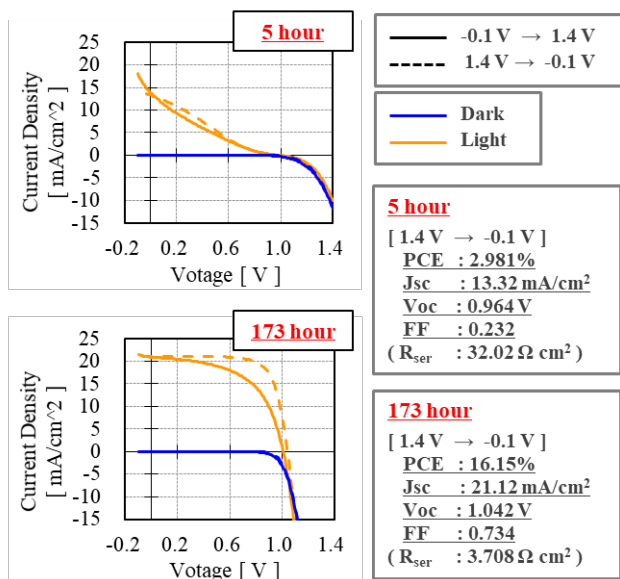


Fig.3 Typical J - V characteristics after exposure to air for 5 hours and after keeping in dry air for 173 hours.

These results indicate that increase of carrier density in DTB occurred due to oxygen-doping. Since HTL was formed in nitrogen atmosphere, oxygen-doping to DTB was probably insufficient after exposure to air for 5 hours.

Secondly, we fabricated PSC devices employing DTB copolymer with BCF dopant. The time dependence of the device performance and the J - V characteristic after exposure to air for 5 hours were shown in Figure 4. When 8.0wt% of BCF was added to DTB, initial J - V characteristics improved. The PCE showed 14.35% and then this value maintained around

14% up to 365 hours. When 4.0wt% of BCF was added to DTB, initial PCE showed 13.56%. Later, the PCE increased to 16.36% after keeping in dry air for 197 hours. The average value of PCE maintained over 14% up to 365 hours.

These results indicate that increase of carrier density in DTB occurred due to BCF-doping. The doping has been explained as for the formation of lewis acid-base adduct [7]. The electrophilic borane of BCF binds to a moiety carrying an accessible lone pair of electrons at the sulfur atoms of the thiophene rings. As a result, hole doping occurred on the thiophene rings of DTB, leading to reduction of R_s . Therefore, the PCE of the device with BCF showed high value compared to that without BCF after exposure to air for 5 hours.

4. Conclusions

We fabricated mesoporous-type PSCs employing DTB copolymer as HTM without and with dopant under nitrogen atmosphere, and measured the device performance in air. In case of the device without dopant, initial PCE showed 2.98% after exposure to air for 5 hours. However, the device performance gradually improved by keeping in dry air. After keeping in dry air for 1 week, PCE greatly improved to 16.15%. These results indicate that increase of carrier density in DTB occurred due to oxygen-doping.

In case of the device with BCF dopant, initial PCE showed 13-14% after exposure to air for 5 hours. The PCE improved to 15-16% by keeping in dry air. The cause of this improvement of the initial device performance was due to increase of carrier density in DTB by BCF dopant.

Acknowledgements

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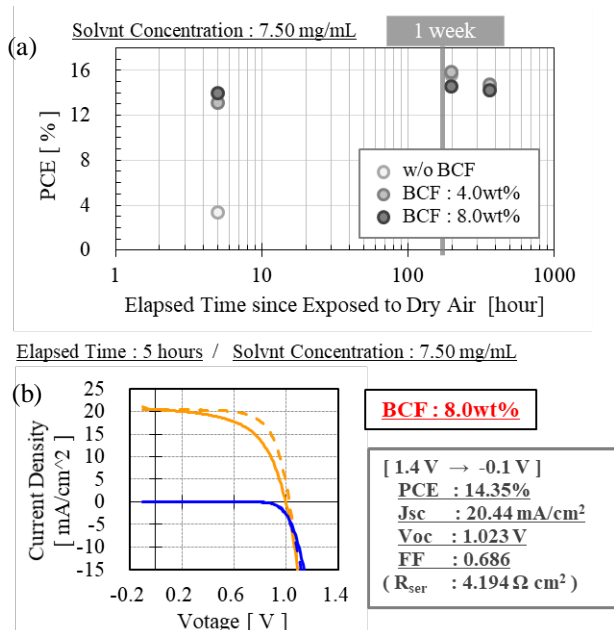


Fig.4 The time dependence of the BCF-doped device performance (a) and the J - V characteristic after exposure to air for 5 hours (b).