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Single-walled Carbon Nanotube Film as Cathode in Flexible Indium-free Planar Heterojunction Perovskite Solar Cells

Il Jeon[1], Takaaki Chiba[2], Clement Delacou[1,2], Yunlong Guo[1], Antti Kaskela[3], Olivier Reynaud[3], Esko I. Kauppinen[3], Shigeo Maruyama[2], and Yutaka Matsuo[1]*

[1]Department of Chemistry, School of Sci.,
The Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-0033, Japan
Phone: +81-3-5841-1476 E-mail: matsuo@chem.s.u-tokyo.ac.jp
[2]Department of Mechanical Eng., School of Eng.,
The Univ. of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan
[3]Department of Applied Physics,
Aalto Univ. School of Sci., 15100, FI-00076 Aalto, Finland

Abstract

In this work, we fabricated indium-free perovskite solar cells (SCs) using direct- and dry-transferred aerosol single-walled carbon nanotube (SWNT). We investigated diverse methodologies to solve SWNT's hydrophobicity and doping issues in SC devices. These include changing wettability of PEDOT:PSS, MoO_3 thermal doping, and HNO_3(aq) doping with various dilutions from 15 to 70 v/v% to minimize its instability and toxic nature. We discovered that isopropanol (IPA) modified PEDOT:PSS works better than surfactant modified PEDOT:PSS as an electrode in perovskite SCs due to superior wettability, while MoO_3 is not compatible owing to energy level mismatch. Diluted HNO_3 (35 v/v%)-doped SWCNT-based device gave the best PCE of 6.32%, which is 70% of an indium tin oxide (ITO)-based device (9.05%). Its flexible application showed 5.38% on a polyethylene terephthalate (PET) substrate.

1. Introduction

Recent emergence of perovskite solar cells have drawn much attention on account of high PCE arising from a long exciton diffusion length of around 100 nm, and a suitable band gap of around 1.55 eV.[1] Similarly, organic SCs have also drawn attention for its low-cost, lightweight, and chemically modifiable nature. However, ITO is indispensible in both types of SCs and its use potentially brings about problems such as lack of supply for mass production and imperfect flexibility for wearable applications.

SWNTs have been regarded as a promising ITO replacement for their mechanical flexibility, abundant carbon composition, easy synthesis, and direct roll-to-roll processability.[2] Recently, the high quality free-standing purely single-walled carbon nanotubes, which are directly transferrable by aerosol chemical vapor deposition, have been developed.[3] This technique can produce SWNT with the transparency of over 90% and the resistance of around 85 $\Omega\,cm^{-2}$. The success of SWNT application in photovoltaics depends on two things: its effective doping in a manner that the dopant does not undermine device performance and overcoming the intrinsic hydrophobicity of SWNTs for uniform film fabrication.

So far, transparent and conductive SWNT film-based organic SCs have been reported in great amount.[4] Yet, analogue applications in perovskite SCs have not been reported to date. Besides, other flexible perovskite SCs reported utilize flexible ITO, which suffers from many shortcomings, such as low conductivity and crack-damage when bent too much.

Here we report SWNT-based indium-free perovskite SCs and flexible application along with investigations of different charge selective layers and doping methods in order to overcome the issues of doping and hydrophobicity of SWNT films. A planar heterojunction structure was used in this study which comprises of PEDOT:PSS as an electron-blocking layer (EBL), followed by perovskite layer ($CH_3NH_3PbI_3$), [6,6]-phenyl C61-butyric acid methyl ester ($PC_{61}BM$), and aluminum metal electrode. Although mesoporous (mp)-TiO_2-based perovskite SC exhibits a higher PCE, the formation of mp-TiO_2 layer requires a thermal process over 450 °C. Since flexible substrates are vulnerable to high temperature, the inverted planar heterojunction perovskite SC, which requires annealing temperature lower than 100 °C, was regarded more promising for our flexible applications.[5] Furthermore, this structure demonstrates better stability under ultraviolet light[6] and hysteresis with sweep directions in measurement because of the exclusion of mp-TiO_2.[7] One-step solution method, which is the most widely established[8], was employed in this work as we focused on achieving reliable investigation prior to record-breaking PCE.

2. General Instructions

One of the challenges for SWNT electrode-based solar cells has been doping the carbon nanotube while having a desirable EBL function. PEDOT:PSS with acidic nature functions as both the EBL and dopant.[9] However, hydrophilic PEDOT:PSS cannot be applied directly to hydrophobic SWNTs. As a solution to this problem, we selected two approaches: diluting PEDOT:PSS in isopropyl alcohol (IPA) solvent by 1:3 (v/v) ratio[10] and adding a small amount (0.5 wt%) of surfactant, polyoxyethylene(6) tridecyl ether to the PEDOT:PSS solution.[11] These two are already well-established methods in the application of graphene and inverted organic SCs, respectively. These modifications change PEDOT:PSS property from hydrophilic to hydrophobic. Both IPA-modified PEDOT:PSS

(IPA-PEDOT:PSS) and surfactant-modified PEDOT:PSS (surfactant-PEDOT:PSS) thoroughly over-coated SWNTs as evidenced by scanning electron microscopy (SEM). During the fabrication, specifically when spin coating a perovskite layer, it was interesting to observe formation of discontinuous large crystals in the perovskite layer on the surfactant-PEDOT:PSS. The cross-sectional SEM revealed a bad uniformity of the perovskite layer. PCEs in the Table 1 shows that the IPA-PEDOT:PSS based device performed better. Therefore we conclude that the IPA-PEDOT:PSS is more compatible with SWNT films in perovskite SCs than the surfactant-PEDOT:PSS.

The compatibility of SWNTs with PEDOT:PSS can also be improved by doping SWNTs with HNO_3 which changes SWNT's property from hydrophobic to hydrophilic. This also entails a one of the strongest doping effect due to strongly acidic nature of HNO_3. However, HNO_3 is toxic and highly reactive.[12] Therefore, HNO_3 was diluted to the extent that its lethal effect is minimized while its doping effective is still retained.

Device performances of the HNO_3-doped SWNT-based perovskite SCs with different HNO_3 concentrations were compared and we observed that all of the HNO_3-doped SWNTs-based perovskite SCs showed much higher PCEs than those of the modified PEDOT:PSS-based SWNTs. It must be mentioned that strong 70 v/v% HNO_3 did not destroy nor undermine the device performance. In addition, there was no stark difference in PCEs until the acid concentration decreases to 15 v/v% where the PCE dropped to 3.88%. 35 v/v% HNO_3 doping was as equally effective as the other highly concentrated HNO_3. Therefore, it can be concluded that HNO_3 (35 v/v%) is the optimum concentration for the application in SWNT-based perovskite SCs.

MoO_3 as an EBL has been commonly used in place of PEDOT:PSS in organic SCs. In fact, MoO_3 is preferred over acidic PEDOT:PSS.[13] However, the same usage has not been witnessed in the field of perovskite SCs. It can be presumed that this is due to its incompatibility in perovskite SCs, but no clear account has been given so far. Since it was reported that thermally annealing MoO_3 can dope SWNTs in a safe and effective manner, we were compelled to check its compatibility in SWNT-based perovskite SCs.[14] Table 1 reveals that both MoO_3-applied and thermally annealed MoO_X-based perovskite SCs performed poorly on both ITO and SWNT film. When PEDOT:PSS and MoO_3 combinations were used in hopes of improving the interface morphology, the photovoltaic performance did not improve. Using photoluminescence and impedance measurement, we found out that the energy mismatching between SWNT and perovskite SCs was the root of this incompatibility.

The best performing structure from this study was selected and perovskite SCs on flexible plastic substrates were fabricated. Polyethylene terephthalate (PET) was used for its high transparency and low-cost merit. A PCE of 5.38% was obtained. (Fig. 1)

Table I Photovoltaic performances of perovskite SCs

Electrode	EBL	V_{OC}	J_{SC}	FF	PCE (%)
ITO	PEDOT:PSS	0.83	16	0.64	9.05
SWNT	IPA-PEDOT:PSS	0.77	11	0.50	4.27
SWNT	Surfactant-PEDOT:PSS	0.61	12	0.38	2.71
70 v/v% HNO_3-SWNT	PEDOT:PSS	0.77	14	0.55	6.09
50 v/v% HNO_3-SWNT	PEDOT:PSS	0.76	15	0.52	5.84
35 v/v% HNO_3-SWNT	PEDOT:PSS	0.79	15	0.54	6.32
15 v/v% HNO_3-SWNT	PEDOT:PSS	0.77	14	0.39	3.88
ITO	MoO_3	0.46	1	0.42	0.12
SWNT	MoO_3	0.37	1	0.28	0.05
SWNT	MoO_x	0.58	13	0.42	2.09

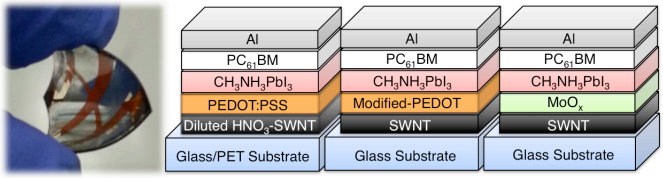

Fig. 1 A picture of flexible application (left) and illustrations of various structures (right)

3. Conclusions

In summary, the three mainstream approaches to SWNT application in perovskite SCs had been viewed. Their compatibility, effectiveness, and mechanism had been studied to understand the uniqueness of perovskite SCs. As non-ITO and SWNT-based perovskite SCs, we anticipate this work can initiate and contribute to the development of ITO-free perovskite SC research. We anticipate these findings will provide better understanding of carbon nanotube application as a transparent conductive electrode in ITO-free perovskite solar cells.

References

[1] M. M. Lee et al., Science **338** (2012) 643.
[2] M. F. L. De Volder et al., Science **339** (2013) 535.
[3] A. Kaskela et al., Nano Lett **10** (2010) 4349.
[4] J. Du et al., Adv. Mater. **26** (2014), 1958.
[5] J.-Y. Jeng et al., Adv. Mater. **25** (2013), 3727.
[6] T. Leijtens et al., Nat. Commun. **4** (2013) 2885.
[7] N. J. Jeon et al., Nat. Mater. **13** (2014) 897.
[8] M. Xiao et al., Angew. Chem. Int. Ed. Engl. **53** (2014) 9898.
[9] E. Kymakis et al., Eur. Phys. J. Appl. Phys. **36** (2006) 257.
[10] H. Park et al., Nano Lett. **14** (2014) 5148.
[11] I. Jeon et al., J. Mater. Chem. A **2** (2014) 18754.
[12] D. W. Shin et al., Nanotechnology **20** (2009) 475703.
[13] J. Meyer et al., Sci. Rep. **4** (2014) 5380.
[14] S. L. Hellstrom et al., Nano Lett. **12** (2012) 3574.