



Multi-walled carbon nanotubes act as charge transport channel to boost the efficiency of hole transport material free perovskite solar cells



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HIGHLIGHTS

- A simple method to embed MWCNTs into perovskite films are reported.
- Perovskite nanoparticles are connected by the MWCNTs.
- Longer electron lifetime is observed.
- Enhanced performance is obtained.

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ABSTRACT

The two-step spin coating process produces rough perovskite surfaces in ambient condition with high humidity, which are unfavorable for the contact between the perovskite film and the low temperature carbon electrode. To tackle this problem, multi-walled carbon nanotubes (MWCNTs) are embedded into the perovskite layer. The MWCNTs can act as charge transport high way between individual perovskite nanoparticles and facilitate the collection of the photo-generated holes by the carbon electrode. Longer carrier lifetime is confirmed in the perovskite solar cells with addition of MWCNTs using open circuit voltage decay measurement. Under optimized concentration of MWCNT, average power conversion efficiency of 11.6% is obtained in hole transport material free perovskite solar cells, which is boosted by ~15% compared to solar cells without MWCNT.

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1. Introduction

Enormous attention has been paid to the field of perovskite solar cells, and extraordinary progress in the power conversion efficiencies (PCEs) has been achieved. PCEs have been improved from the initial 3.8% in 2009 to a certified 22.1% in about seven years [1,2]. This explosive development is unprecedented and the benefits of solution process together with high efficiencies make perovskite solar cell a strong challenger to the established silicon based solar cells. To achieve PCEs around 20% in perovskite solar

cells, hole transport material (HTM), usually spiro-OMeTAD, and noble metal electrode, usually Au or Ag, are used [3,4]. Although amazing performances are observed, the main drawbacks are the stability issue related with the organic HTM and the high fabrication cost originating from expensive HTM and the high vacuum instrument needed to deposit the noble metal electrode [4–6]. In order to cut down the fabrication cost and pursue long term stability, HTM free perovskite solar cells with carbon counter electrode are proposed [7–11]. This kind of solar cells utilize the ambipolar transport property of perovskite. The photo-generated charge carriers are separated at the metal oxide (e.g. TiO₂) and perovskite interfaces, electrons are collected by the metal oxide film, while holes transport through the perovskite particles and are extracted by the carbon counter electrode. PCEs approaching 15% have been reported [8,9], making this low cost and highly stable HTM free perovskite solar cells a promising member in the family of

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perovskite solar cells.

Carbon based HTM free perovskite solar cells are commonly fabricated using two different strategies. The first strategy is to sequentially deposit a TiO₂ scaffold layer, a ZrO₂ or Al₂O₃ insulating layer, and a mesoporous carbon layer. Then perovskite precursor solution is infiltrated through the top carbon layer [7,12,13]. The main problem is that the perovskite precursor solution is difficult to infiltrate into all the three layers. In addition, the carbon layer needs to be sintered at high temperature. The other strategy is to adopt a low temperature carbon paste [10,14,15]. The perovskite light absorb layer can be prepared using one-step spin coating or two-step spin coating process. Subsequently, the carbon paste is screen-printed or doctor-bladed onto the perovskite film and annealed at 100 °C to complete the fabrication of a perovskite solar cell. This method is simple, low cost, and compatible with flexible solar cells and roll-to-roll production. The key point limiting the PCEs of this kind of perovskite solar cells is the poor contact at the perovskite and carbon interfaces [10,16–18]. The commonly adopted two-step spin coating process produces nano-cuboid shaped perovskite particles with a large variation in the sizes, leading to a rough perovskite surface with convex-concave features. This makes it difficult for the low temperature carbon paste to intimately contact with the perovskite nanoparticles, especially when large sized graphite flakes exist in the carbon paste [17]. In this case, photo-generated holes need to transport longer distances before they can be collected by the carbon electrode, leading to high risk of recombination and low PCE. Much effort has been made to improve the contact between the perovskite film and the carbon electrode. The main composition of the carbon paste (carbon black and graphite flake) and their individual sizes influence the contact at the perovskite and carbon interface thus can be optimized to obtain higher PCEs [8,16]. Improvement in the interface quality between perovskite film and carbon electrode could also be obtained using in situ chemical transformation process with the addition of CH₃NH₃I into the carbon paste [10]. Solvent engineering process to obtain smooth perovskite film is also a method to tackle the contact problem and boost the efficiency to beyond 14% [9].

Single-walled carbon nanotube (SWCNT) and multi-walled carbon nanotube (MWCNT) exhibit excellent charge transport property and chemical stability. Their mixtures with TiO₂ nanoparticles have been widely used to prepare the photoanode for dye-sensitized solar cells [19–21]. The addition of highly conductive carbon nanotube (CNT) in the photoanode can improve both charge separation and electron transport in the devices, thereby improving the performance of the solar cells. Recently, various applications of CNT in the emerging perovskite solar cells have been reported. The widely used HTM in perovskite solar cells, i.e., spiro-OMeTAD, exhibits intrinsically low hole mobility, and needs to be doped with lithium salts to increase the charge mobility, which will cause possible stability problem in the perovskite solar cells. Incorporation of CNT into the spiro-OMeTAD layer has been demonstrated to be a brilliant method to enhance the hole mobility, improve the PCE, and bypass the possible stability problem [22,23]. CNT can also be applied as counter electrode in HTM free perovskite solar cells. Highest fill factor (FF) of 80% has been observed in HTM free perovskite solar cells using MWCNT as counter electrode [17]. PCE of 14.7% has also been reported using SWCNT and carbon composite as counter electrode, which is among the highest PCEs reported in HTM free perovskite solar cells [8].

Here, we present a simple and facile method to improve the interfacial contact between perovskite film and low temperature carbon electrode using MWCNT in ambient conditions with relatively high humidity ($\geq 50\%$). The MWCNTs are embedded into the perovskite film and act as a high way for charge transportation between two individual perovskite nanoparticles. The photo-

generated holes can easily transport along the MWCNTs to the nearest perovskite nanoparticles that are intimately connected to the low temperature carbon electrode, and be collected by the carbon electrode. Therefore, the charge collection efficiency is expected to be enhanced, leading to improvement in the open circuit voltage (V_{oc}), short circuit current (J_{sc}), FF and the corresponding PCE. With addition of 0.1 mg mL⁻¹ MWCNT in the PbI₂ DMF solution, average PCE of 11.6% is obtained, which is enhanced by about 15% compared to HTM free perovskite solar cells without MWCNT.

2. Experiments

2.1. Fabrication of the HTM free perovskite solar cell

HTM free perovskite solar cells with a low temperature carbon electrode are fabricated under ambient condition with a relatively high humidity ($\geq 50\%$) according to our previous reports [15,24,25]. In brief, a 0.15 M titanium diisopropoxide bis(acetylacetonate) in 1-butanol is spin-coated onto the pre-etched and cleaned FTO glass at 3000 rpm for 30 s, then followed by heat treatment process at 150 °C for 30 min in the air. A homemade P25 paste is spin-coated successively at 3000 rpm for 30 s and heated at 500 °C for 30 min. The TiO₂ films are further treated with a 40 mM TiCl₄ aqueous solution at 70 °C for 30 min then washed with deionized water and ethanol. A SiO₂ paste, which is prepared according to our previous report [25] and diluted in ethanol with a weight ration of 1:3, is spin-coated on the TiCl₄ treated film at 3000 rpm for 30 s and heated at 500 °C for 30 min. Commercial MWCNT (OD: 30–50 nm, Length: 10–20 μ m, XFNANO, INC) is dispersed into DMF using an ultrasonic probe with a desired concentration. 1.0 M PbI₂ and 0.2 M PbCl₂ are then dissolved into the DMF at 70 °C under stirring. The prepared PbI₂ precursor is spin-coated onto the TiO₂/SiO₂ scaffold layer, treated with ethanol and dried at 100 °C for 15 min CH₃NH₃I isopropanol solution (7 mg mL⁻¹) is loaded onto the PbI₂ film for 5 min and then dried with flowing nitrogen gas. The obtained perovskite film is further dried at 100 °C for 15 min. Finally, a low temperature carbon electrode is doctor-bladed onto the perovskite film.

2.2. Characterization

Crystal phase of the perovskite films are measured using X-ray diffraction (XRD) instrument (Bruker D8) with Cu K α radiation ($\lambda = 0.1542$ nm). UV–vis absorption are recorded on Lambda 650S, PerkinElmer. Scanning electron microscopy (SEM) images are obtained from Sirion FEG, USA. J-V measurement of the solar cells is carried on a CHI660C electrochemical workstation under AM 1.5 illumination at 100 mW cm⁻². A scan rate of 0.05 V s⁻¹ is used. Effective area of the solar cells is kept to 0.1 cm² with a mask.

3. Results and discussion

It is difficult to prepare high quality CH₃NH₃PbI₃ perovskite films under high humidity. Usually a large amount of residual PbI₂ exists in the film, which is detrimental to the PCEs of the solar cells. Solvent treatment process has been demonstrated to be a facile strategy to lower down the PbI₂ amount [24]. Thus the PbI₂ films are treated with ethanol in this work and X-ray diffraction (XRD) measurements are taken to check the crystal structure of the resultant perovskite films. XRD patterns of the pristine perovskite film and perovskite film with the addition of 0.1 mg mL⁻¹ MWCNT are presented in supporting information Fig. S1. The diffraction peaks marked by the diamonds can be assigned to the characteristic diffraction peaks of the tetragonal CH₃NH₃PbI₃ perovskite. The diffraction peak corresponding to PbI₂ at about 12.6° is negligible,

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