Research paper

Evidence for reduced charge recombination in carbon nanotube/perovskite-based active layers

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ABSTRACT

Using impedance spectroscopy and computation, we show that incorporation of multi-walled carbon nanotubes (MWCNTs) in the bulk of the active layer of perovskite-based solar cells reduces charge recombination and increases the open circuit voltage. An ∼87% reduction in recombination was achieved when MWCNTs were introduced in the planar-heterostructure perovskite solar cell containing mixed counterions. The open circuit voltage (V_{oc}) of perovskite/MWCNTs devices was increased by 70 mV, while the short circuit current density (J_{sc}) and fill factor (FF) remained unchanged.

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1. Introduction

Lead halide-based perovskite solar cells [1–9] have garnered widespread attention because of their high efficiency [10,11] and low-temperature solution processing [12]. Over the past few years there have been numerous reports on perovskite solar cells, especially on materials processing [4,13] and interface engineering [10,14], to enhance device efficiency. A key feature of lead trihalide-based perovskites is that they are ambipolar charge transporters [5,15]. Upon photo-illumination, photo-generated carriers, i.e., electrons and holes, get transported through the same active layer. Thus, although the mobilities of the charge carriers are high in the perovskite layer, inefficient charge extraction out of the active layer leads to charge recombination [16,17] in the bulk, which lowers the open circuit voltage (V_{oc}). Theoretical calculations predict that the open circuit voltage can be increased by 60 mV if the charge recombination losses are reduced by an order of magnitude [18]. Thus, perovskite solar cells require either an electron- or a hole-transporting layer or both for selective charge

extraction at the perovskite/electrode interfaces [19]. In a conventional device, a compact or a nanostructured/mesoporous TiO_2 layer is used as the electron transporting material (ETM), which extracts the electrons from the perovskite layer and reduces the charge recombination [16,20,21]. 2,2′,7,7′-tetrakis(N,N-di-p-methoxyphenylamine)-9,9′-spirobifluorene (spiro-OMeTAD) is commonly used as the hole transporting material (HTM) [22]. In an inverted device architecture, a thin layer of poly(3,4-ethylenedioxythiophene) polystyrene sulfonate (PEDOT:PSS) is placed between the ITO electrode and the active layers to extract the holes. A [6,6]-phenyl-C_{61}-butyric acid methyl ester (PCBM) layer is placed between the metal electrode and the perovskite layer to extract the electrons [11,12]. Except for mesoporous TiO_2, all other methods focus on the extraction of charges at the interface and not in the bulk. Moreover, the electron and hole mobilities in PCBM and PEDOT:PSS, respectively, are very low compared to those in the perovskite active layer. Modifications to PCBM [23] or PEDOT:PSS layers [24] are necessary to increase the electron or hole extraction rate. Nanostructured carbon [25], including CNTs and graphene based systems, has been used for a variety of energy applications particularly transparent electrodes and charge transport layers [26]. CNTs have been used in composite materials as electrodes for perovskite devices [27,28]. Also, CNTs have been incorporated at the perovskite-electrode interface [29–34], which helps with hole extraction at the interface. In principle, one can extend this concept to extract holes from the bulk also if CNTs are incorporated into the active layer. However, this has been a challenge because it

has been difficult to obtain stable CNT dispersions in solvents that are compatible with perovskite active layer fabrication. Herein, we show the facile incorporation of MWCNTs in the bulk of the perovskite layer and the reduction in recombination losses by 87%. We also demonstrate that the introduction of MWCNTs in the bulk of the perovskite layer reduces the charge accumulation at the perovskite/PEDOT:PSS interface and leads to improved V_{oc} and thus higher power conversion efficiency (PCE).

2. Materials and methods

Stable dispersions of MWCNTs were prepared in N,N-dimethylformamide (DMF) as shown in Fig. 1. For this study, we used MWCNTs that have outer diameters of 40–60 nm and lengths of 1–2 μm. First, MWCNTs were added to DMF (0.1 mg mL^{-1}) along with poly(methyl methacrylate) (PMMA)-functionalized hexaben-zocoronene (HBC). The HBC moiety was placed specifically at the PMMA chain-end such that the polymer chain-end can interact with the MWCNT through strong π-π interactions [35]. The dispersion was then ultrasonicated for a few minutes and was allowed to

settle for 24 h before use. MWCNTs that were not attached to the polymer settled at the bottom of the vial and were separated from the dispersion by decantation. The dispersion is stable over 30 days under ambient conditions (see Fig. S1).

Planar heterojunction perovskite solar cells were fabricated in air by sequential deposition [13] of organic counterions onto the PbI$_2$ thin film. 50 μL of hot solution (400 mg mL^{-1}) of lead iodide in DMF was spin coated on a pre-heated (85 °C) PEDOT:PSS-coated ITO substrate at 6000 rpm for 35 s. PbI$_2$-coated substrates were then annealed at 85 °C for 45 min. Mixed counterions (1:1 by wt. ratio) of methylammonium iodide (MAI) and formamidinium iodide (FAI) were dissolved in isopropanol (40 mg mL^{-1}). 50 μL of this solution was spin coated on top of PbI$_2$ films at 6000 rpm for 35 s at room temperature. Devices were then annealed at 85 °C for 45 min in the dark. MWCNT/perovskite composite devices were prepared from the PbI$_2$ solution containing 0.005% and 0.01% of MWCNTs (by wt. to PbI$_2$) in DMF keeping the PbI$_2$ concentration approximately 400 mg mL^{-1}. Powder X-ray diffraction (PXRD) revealed (see Fig. S2) complete conversion to a trigonal (*P3m1*) perovskite phase for films fabricated with or
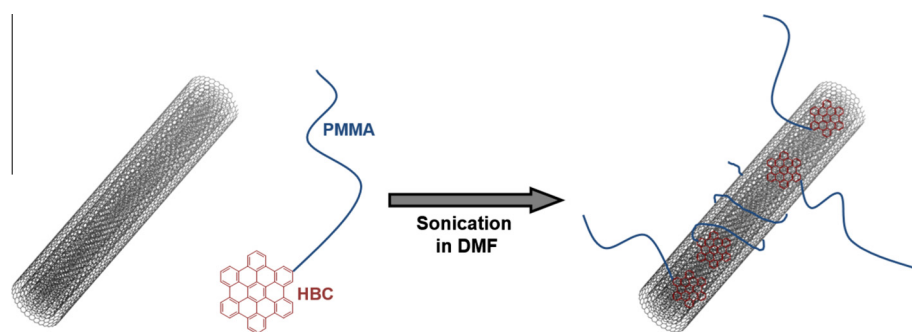

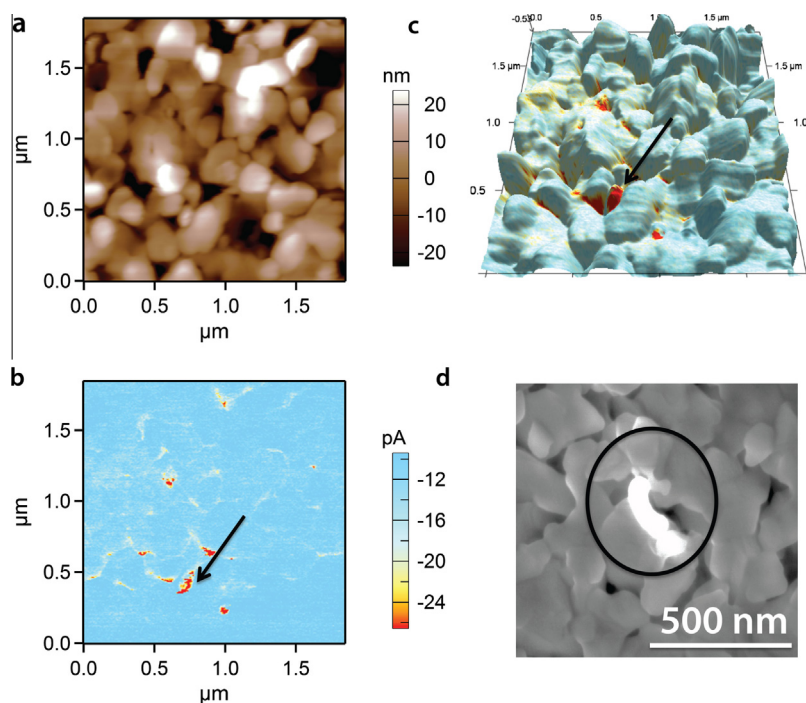**Fig. 1.** Schematic representation of HBC-PMMA-grafted MWCNT.

Fig. 2. (a) AFM topographic image of PbI$_2$/MWCNT composite film on PEDOT:PSS-coated ITO substrate. (b) cAFM image of the same area. (c) Topographic image superimposed onto current mapping from cAFM. High current regions are from MWCNTs. (d) SEM image of PbI$_2$/MWCNTs composite film on Si substrate. A MWCNT is highlighted with a circle.