Supporting information for

Enhanced Grain Size of Organic Halide Perovskite by Sulfonate-Carbon Nanotubes Incorporation for High Performance Perovskite Solar Cells

Yong Zhang[a], Licheng Tan[a,b], Qingxia Fu[a], Lie Chen[a,b], Ting Ji[a], Xiaotian Hu[a] and Yiwang Chen*[a,b]

[a]College of Chemistry/Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

[b]Jiangxi Provincial Key Laboratory of New Energy Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

Corresponding author. Tel.: +86 791 83968703; fax: +86 791 83969561. E-mail: ywchen@ncu.edu.cn (Y. Chen)

Experimental section

Synthesis of sulfonated carbon nanotubes. Pristine multiwall carbon nanotubes (diameter 40–60 nm, XFNano Materials Nanjing, China) were sonicated in the mixture of 1:1 concentrated HNO_3 (65%) and HCl (37%) for 1 h, these steps can remove catalyst particles around CNTs and also introduced oxygen-containing groups, mainly carboxyl groups on the CNTs. We defined them as f-CNTs in the following text. The f-CNTs were filtered and washed for times, then dried at 120 ºC in the vacuum overnight. Then 60 mg concentrated H_2SO_4 (98%) and 80 mg f-CNTs were mixed in a dry flask and then sonicated for 1 h, followed by heating to 260-300 ºC (The sulfuric acid boils at 335.5 ºC) with an electrical hand blender under nitrogen atmosphere for 20 h. After this treatment, the suspension was diluted by water and filtered. The production were washed to remove excess acid and frozen in a refrigerator, then dried in a vacuum refrigerant dryer for 24 hours to obtain sulfonated CNTs (s-CNTs).

Perovskite Precursor Preparation. The perovskite precursor solution was prepared by dissolved lead (II) iodide (PbI_2, Sigma-Aldrich, 99%) and Methylamine iodide (MAI, TCI, 99%) (molar ratio 1:1) in anhydrous N,N-dimethylformamide (DMF, Sigma-Aldrich) with final concentrations of 40 wt%. s-CNTs were fabricated as the literature reported. The s-CNTs we prepared can be readily dispersed in DMF (>2 mg ml^{-1}). Appropriate scale CNTs or s-CNTs were added into the precursor solution with the concentration of 0.05 mg ml^{-1}. Concentrations of 0.02 mg ml^{-1}, 0.1 mg ml^{-1} and 0.2 mg ml^{-1} s-CNTs were add in the precursor solution as reference samples. The solution was stirred at 60 °C overnight in argon glovebox. The solution was filtered with a 0.45 μm polyvinylidene fluoride filter before use.

Device Fabrication. The perovskite solar cells were fabricated on F-doped indium oxide (FTO) pattern glass substrates (Zhuhai Kaivo Optoelectronic Technology Co., Ltd. <15 Ω) with the following device configuration: FTO/b-TiO_2/mp-TiO_2/$CH_3NH_3PbI_3$/spiro-MeOTAD/MoO_3/Ag. First, the FTO glass substrates were cleaned by sequential ultrasonic treatment in detergent, acetone, deionized water, and isopropyl alcohol for 15 min each and then dried with a nitrogen stream. Then the precleaned FTO glass substrates were treated by ultraviolet (UV)-ozone for 20 min in UV chamber. A 30 nm thick TiO_2 blocking layer was sequentially spin coated twice from a solution containing 0.3 M in n-butyl alcohol. The mesoporous TiO_2 layer was spin coated from a solution containing 1 g 18NRT Dyesol paste in 7 ml of EtOH at 5000rpm for 30 s. And the TiO_2 coated substrates were annealing at 500 ºC for 30 min. The $CH_3NH_3PbI_3$ perovskite film was fabricated by the fast deposition-crystallization procedure as described elsewhere.[1] Typically, perovskite precursor solution was spin-coated on the mesoporous TiO_2 layer at 5500 rpm in glove box. During the perovskite precursor solution spin-coating process, 150 μL chlorobenzene was quickly added on the surface of the substrate after a specific delay time of 6 s. Prepared perovskite precursor solutions were deposited inside a argon glovebox (MBraun) and annealing at 100 ºC for 10 min. HTM solution was prepared by mixing 75 mg ml^{-1} spiro-OMeTAD, 28 μl tert-butylpyridine and 18 μl of bis(trifluoromethane) sulfonamide lithium salt (Li-TFSI) solution (520 mg in 1 ml acetonitrile) in 1 ml chlorobenzene. The HTM solution was spin-coated onto the perovskite film at 3000 rpm for 30 s. The substrates were kept in a desiccator overnight. Finally, a 100 nm thick Ag anode (thermal deposition rate of 1.0 Å/s) was deposited on the substrate through a shadow mask to give a device area of 0.06 cm^2 under a vacuum level of 10^{-4} Pa. All devices measurements were performed in an ambient environment (below 25% humidity) at room temperature.

Device Characterization. The illuminated current density-voltage (*J-V*) characteristics were characterized using Keithley 2400. The currents were measured under 100 mW cm^{-2} simulated AM 1.5 G irradiation (Abet Solar Simulator Sun2000). The incident photon-to-current conversion efficiency (IPCE) spectrum was detected under monochromatic illumination (Oriel Cornerstone 260 1/4 m monochromator equipped with Oriel 70613NS QTH lamp), and the calibration of the incident light was performed with a monocrystalline silicon diode. Scanning electron microscopy (SEM) imaging was conducted on SU8020 scanning electron microscope operated at an acceleration voltage of 8 kV. X-ray diffraction (XRD) measurements were performed with a Rigaku D/Max-B X-ray diffractometer with Bragg-Brentano parafocusing geometry, a diffracted beam monochromator, and a conventional cobalt target X-ray tube set to 40 KV and 30 mA. The ultraviolet-visible (UV-vis) spectra of the samples were recorded on a PerkinElmer Lambda 750 spectrophotometer. The photoluminescence spectra were measured by photoluminescence spectroscopy (Hitachi F-7000). Time-resolved photoluminescence were measured by an Edinburgh Instruments FLS920 spectrometer. X-ray photoelectron spectroscopy (XPS) studies were performed on a Thermo-VG Scientific ESCALAB 250 photoelectron spectrometer using a monochromated Al (Ka) (1486.6 eV) X-ray source. Fourier transform infrared (FTIR) spectra were recorded on Shimadzu IRPrestige-21 spectrometer.

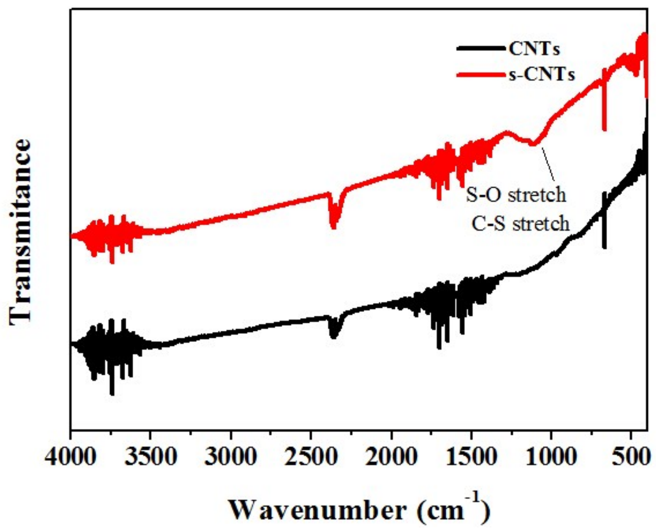

Figure S1. FTIR spectra of the pristine CNTs and s-CNTs.

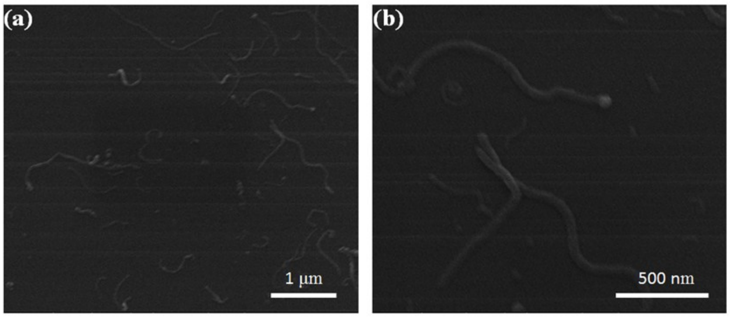

Figure S2. (a) Low- and (b) high-magnification scanning electron microscope images of s-CNTs.

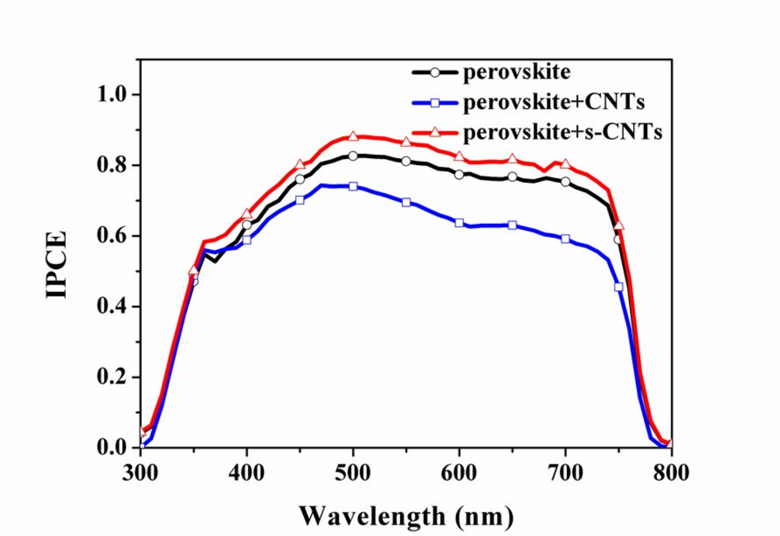

Figure S3. Incident photon-to-current conversion efficiency (IPCE) spectra for $CH_3NH_3PbI_3$, CNTs incorporated $CH_3NH_3PbI_3$ and s-CNTs incorporated $CH_3NH_3PbI_3$ perovskite solar cells with the configuration glass/FTO/c-TiO_2/mp-TiO_2-$CH_3NH_3PbI_3$ nanocomposite layer/$CH_3NH_3PbI_3$ upper layer/spiro-MeOTAD/Ag. The calculated current density are 18.5 mA cm^{-2}, 15.5 mA cm^{-2} and 19.7 mA cm^{-2}, respectively.

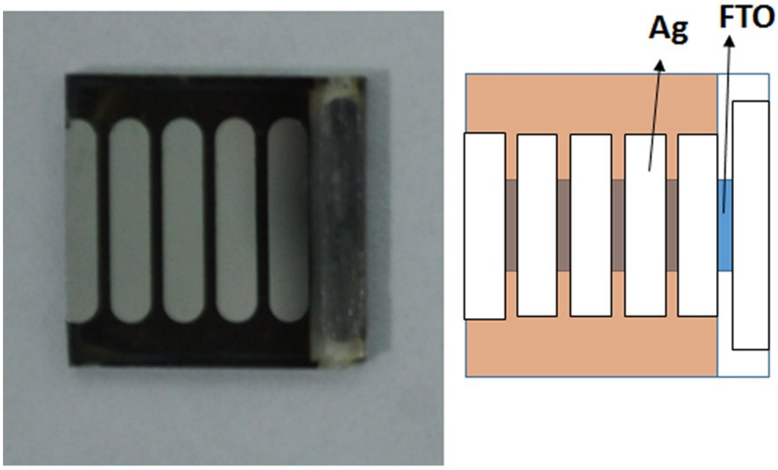

Figure S4. The picture and related schematic diagram of the fabricated perovskite solar cell with the structure of glass/FTO/c-TiO_2/mp-TiO_2-$CH_3NH_3PbI_3$ nanocomposite layer/$CH_3NH_3PbI_3$ upper layer/spiro-MeOTAD/Ag. For the edge effect of the substrate, the performance of the edge device is often much lower than others.

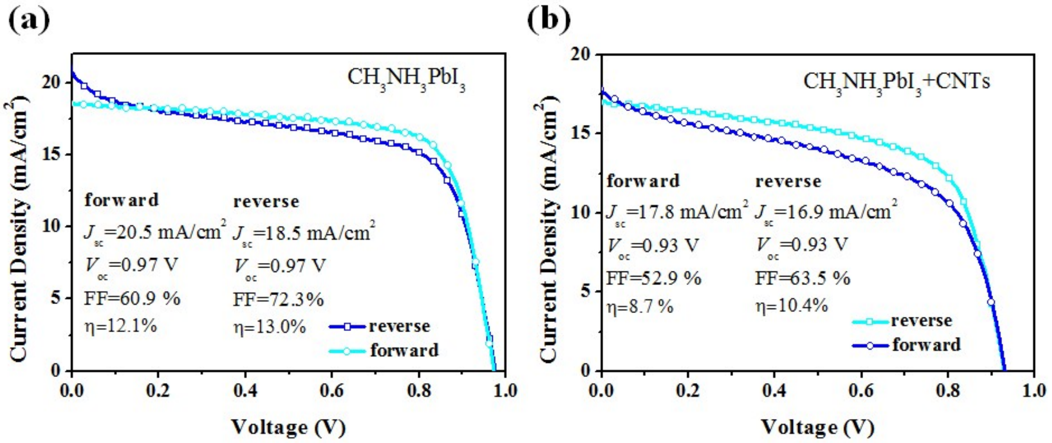

Figure S5. Forward and reverse scan *J*-*V* curves for $CH_3NH_3PbI_3$ and CNTs doped $CH_3NH_3PbI_3$ perovskite solar cells.

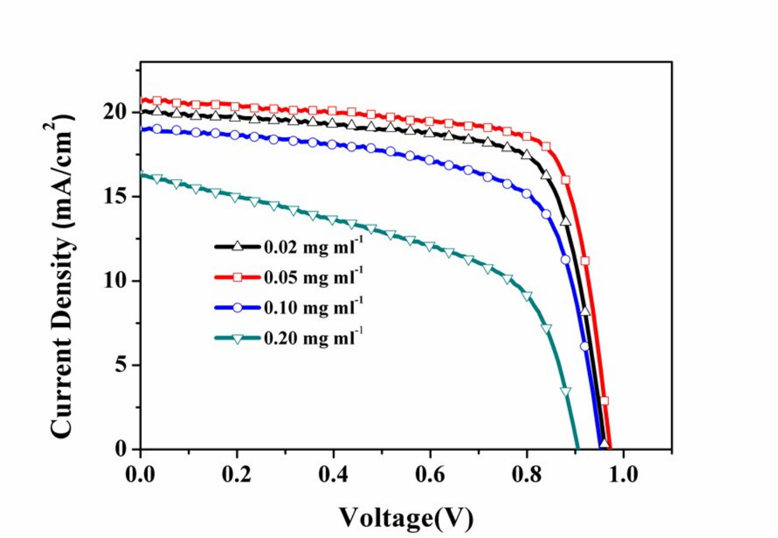

Figure S6. *J-V* characteristics for the perovskite solar cells fabricated with different concentrations of s-CNTs in precursor solution.

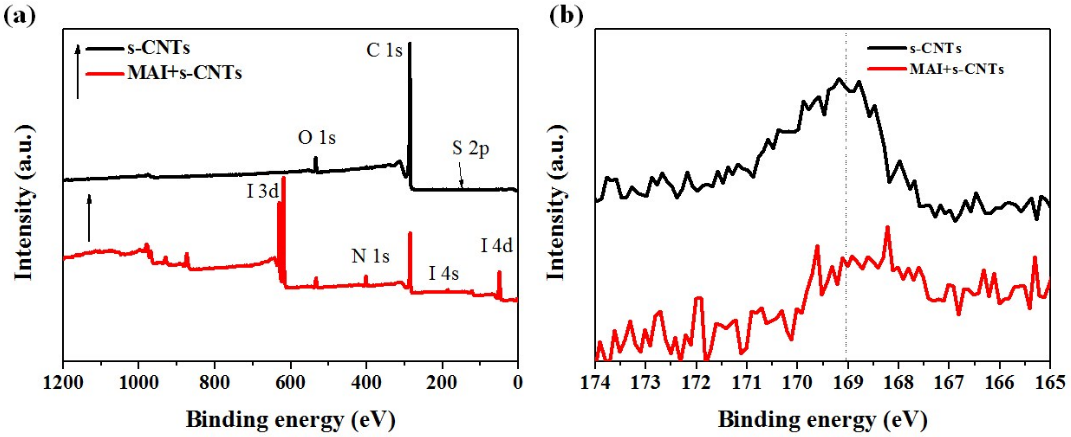

Figure S7. (a) XPS survey spectra of s-CNTs and s-CNTs doped perovskite, (b) S 2p response in XPS spectra of s-CNTs and s-CNTs doped perovskite.

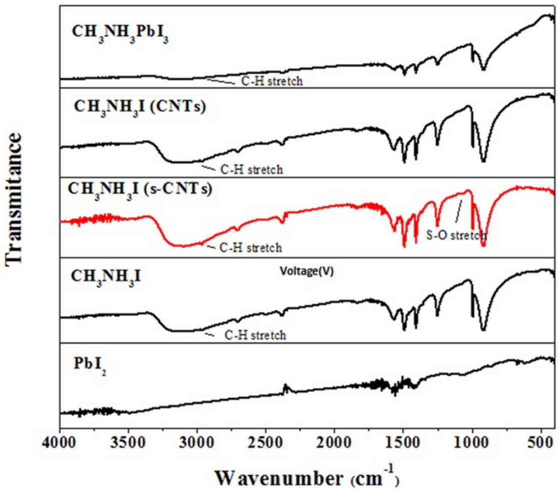

Figure S8. FTIR spectra of PbI_2, MAI, MAI (CNTs), MAI (s-CNTs) and $MAPbI_3$ powders.

Table S1. Photovoltaic parameters of the cells fabricated as a function of $MAPbI_3$ and CNTs or s-CNTs added in $MAPbI_3$.

Device	Active layer	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	Best PCE (%)	Deviation (%)
A	$CH_3NH_3PbI_3$	19.1	0.95	68.8	12.5	11.2±1.2
B	$CH_3NH_3PbI_3$+CNTs	17.8	0.93	62.0	10.3	8.6±2.5
C	$CH_3NH_3PbI_3$+s-CNTs	20.8	0.97	75.1	15.2	14.5±0.9

Table S2. Photovoltaic parameters of the cells fabricated with different concentrations of s-CNTs in precursor solution.

Concentration (mg ml^{-1})	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
0.02	20.0	0.96	72.7	13.9
0.05	20.6	0.97	75.0	15.0
0.10	18.9	0.95	67.2	12.1
0.20	16.2	0.90	53.1	7.8

Reference

1. M. Xiao, F. Huang, W. Huang, Y. Dkhissi, Y. Zhu, J. Etheridge, A. Gray-Weale, U. Bach, Y.-B. Cheng and L. Spiccia, *Angew. Chem. Int. Edit.*, 2014, **126**, 10056-10061.