Interface Connection of Functionalized Carbon Nanotubes

for Efficient and Stable Perovskite Solar Cells

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Materials for PSCs fabrication:

4-Tertbutylpyridine (tbp), bis(trifluoromethane) sulfonamide lithium salt, and FK209 [tris(2-(1H-

pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis(trifluoromethylsulfonyl) imide)], chlorobenzene (CB), dimethylsulphoxide (DMSO), isopropanol (IPA) and dimethylformamide (DMF) were supplied from Sigma-Aldrich. PEAI, FAI, MAI and $PbBr_2$ were purchased from GreatCell Solar. Lead iodide was purchased from Alfa Aesa. Spiro-OMeTAD was purchased from Merck. The SnO_2 nanoparticle was supplied from Alfa Aesa. All of the purchased chemicals were used as received without further purification.

Device fabrication:

The chemically etched FTO glass (Nippon Sheet Glass) was cleaned with a detergent solution, acetone, and ethanol. SnO_2 nanoparticle was diluted in deionized water with a volume ratio of 1:4 and coated on the FTO substrate at a speed of 3000 rpm for 20 s with a ramp-up of 2000 rpm s^{-1}, finally heating at 150 °C for 10 min; The CNT layer was dispersed in DMF with various concentrations and dynamic spin-coating on the SnO_2 layer at a speed of 4000 rpm for 20 s with a ramp-up of 3000 rpm s^{-1} finally heating at 100 °C for 10 min, and then perovskite solutions (The molar ratio of PbI_2, MAI, FAI, $PbBr_2$ is 1: 0.16: 0.84: 0.11, the molar of PbI_2 is 1.38 mmol/mL, the MACl is 0.305 mmol/mL which added in to the perovskite solution; The solvent is composed by DMSO and DMF with a ratio of 1:4) are successively spin-coated on the substrates at 1000 rpm for 10s and 5000 rpm for the 30s, respectively. 200 µL of chlorobenzene was dropped in 10 s at 5000 rpm. Perovskite films were annealed at 150 °C for 10 min. The 10 mg PEAI was dissolved in 1 mL IPA and spin-coated on perovskite film at 3000 rpm for the 20s. The HTM solution was prepared by dissolving 75 mg of Spiro-OMeTAD (Merck) with additives in 1 mL of chlorobenzene. As additives, 18 µL of Li-bis(trifluoromethanesulfonyl) imide from the stock solution (520 mg in 1 mL of acetonitrile), 13 µL of FK209 [tris(2-(1H-pyrazol-1-yl)-4-tert-butylpyridine)-cobalt(III) tris(bis (trifluoromethylsulfonyl)imide) (375 mg in 1 mL of

acetonitrile), and 30 µL of 4-tert-butylpyridine were added. The Spiro-OMeTAD layer was formed by spin-coating the solution at 4000 rpm for 20 s and followed by the deposition of the 70 nm thick Au electrode by thermal evaporation.

Devices and films Characterization:

For the PL lifetime measurements, samples are excited with a 408 nm pulsed laser (MDL 300, PicoQuant) with 40 µm cm^{-2} pulse energy density. The current density-voltage (J−V) curves of electron-only devices and photovoltaic devices were measured using a Keithley 4200-SCS semiconductor parameter analyzer. The photovoltaic devices were measured under AM 1.5 G one sun illumination (100 mW/cm^2) with a solar simulator (Newport 94021A) calibrated by a Si-reference cell certified by NREL. The cells were masked with the active area of 0.09 cm^2 to fix the active area and reduce the influence of the scattered light for the small device. All measurements were characterized at room temperature in the air. IPCE spectra were recorded as a function of wavelength under a constant white light bias of ≈10 mW cm^{-2} supplied by an array of white light emitting diodes. The excitation beam from a 300 W xenon lamp (ILC Technology) was focused through a Gemini-180 double monochromator (Jobin Yvon Ltd) and chopped at ≈ 2 Hz. The signal was recorded using a Model SR830 DSP Lock-In Amplifier (Stanford Research Systems).

DFT calculations:

The calculation of geometry optimization of CNT was performed by the Gaussian 09W program using the B3LYP exchange-correlation functional.[1] The calculation was performed by Vienna Ab-initio Simulation Program (VASP) package by employing a PAW-PBE pseudopotentials.[2-4] The optimizations of the lattice constants and the atomic coordinates were made by the minimization of

the total energy with k-points of $2 \times 2 \times 2$. All the atoms were allowed to relax until all internal atomic forces were within 0.005 eV/Å, and the plane-wave cutoff energy was set as 600 eV.

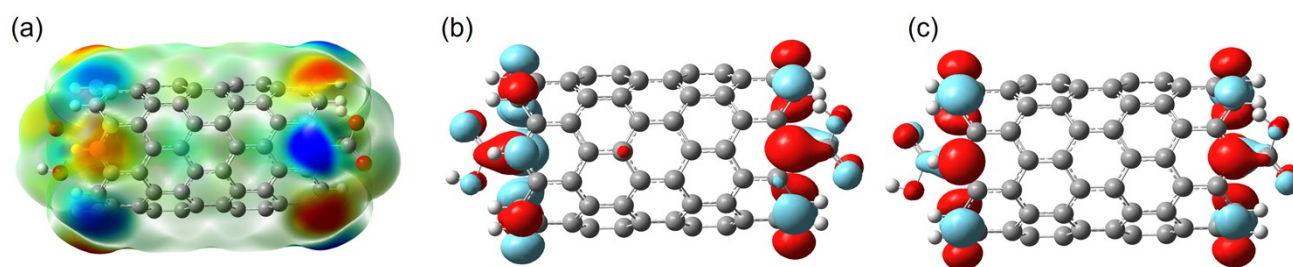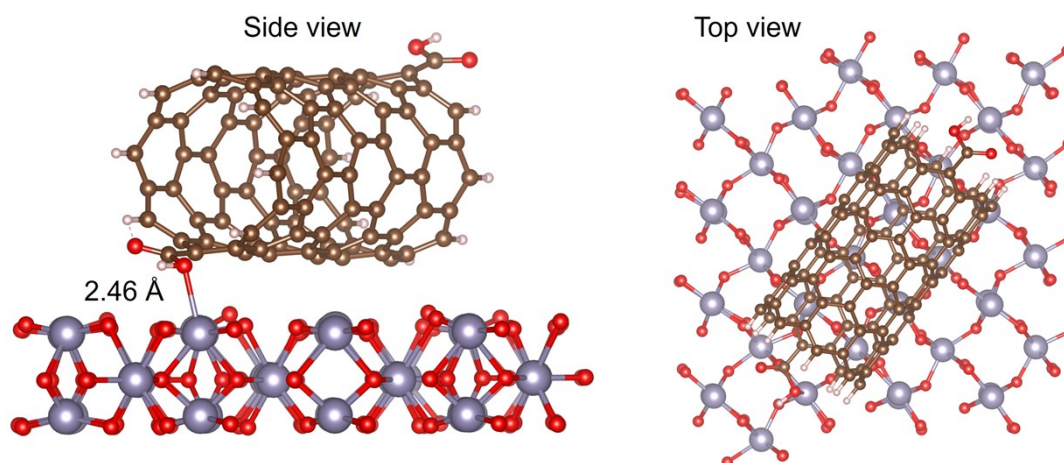Figure S1. The optimized geometry of CNTs and it electronic properties. (a) ESP; (b) LUMO; (c) HOMO.

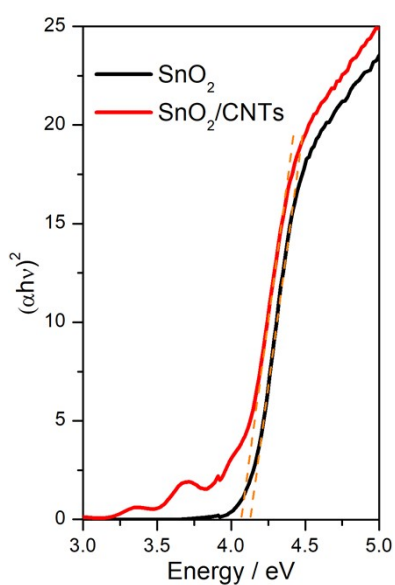Figure S2. The optimized geometry of CNTs interacted with SnO_2 (001) surface.

Figure S3. Tauc plots of SnO_2 films with or without the CNTs modification.

Table S1. Fitting parameters of *bi*-exponential decay function in TRPL of FTO/SnO$_2$/Perovskite with or without the CNT modification.

Films	Fraction A$_1$	τ_1 (ns)	Fraction A$_2$	τ_2 (ns)	Average decay time τ (ns)[a]
FTO/SnO$_2$/Perovskite	54.7%	4.5	45.3%	221.5	216.3
FTO/SnO$_2$/CNT/Perovskite	52.6%	3.5	47.4%	150.1	146.5

[a] Average decay time is calculated according to the equation: $\tau = (A_1\tau_1^2 + A_2\tau_2^2)/(A_1\tau_1 + A_2\tau_2)$.

Table S2. The details photovoltaic parameters of PSCs with or without the CNT modification under the reverse and forward scans.

CNTs	J_{sc} [mA cm^{-2}]	V_{oc} [V]	FF	PCE [%]
0 mg/mL Reverse	24.90	1.122	0.807	22.54
0 mg/mL Forward	24.95	1.095	0.796	21.74
0.07 mg/mL Reverse	24.95	1.161	0.830	24.04
0.07 mg/mL Forward	24.99	1.145	0.823	23.54

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