Supporting Information

"Metal-free hole-conductor-counter electrode based on carbon nanotubes for high efficiency perovskite solar cells"

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Single-walled carbon nanotube film synthesis

The single-walled carbon nanotube (SWCNT) film was synthesized by a pilot-scale aerosol chemical vapor deposition method described elsewhere[1]. In short, a ferrocene-containing $CO:CO_2$ (ratio 99:1) gas was directed into a tube furnace at temperature of 880 °C. The ferrocene decomposes in the furnace and forms aerosol particles, which function as catalysts for the SWCNT growth. The SWCNT bundle-containing gas is directed out from the reactor outlet through a porous filter paper, on which the film is formed.

SWCNT film sample preparation for characterization

The SWCNT film characterization was carried out on films deposited on quartz substrates. The studied film types were pristine SWCNT film, SWCNT film densified with chlorobenzene

and SWCNT:Spiro-OMeTAD film (see below). For the latter two films, also double layer films were studied, since two layers were used also in the solar cells.

Solar cell manufacturing

Fluorine-doped tin oxide (FTO) glass (Nippon Sheet Glass, 10 Ω/sq) was cleaned by sonication in 2 % Hellmanex water solution for 30 minutes. After rinsing with deionised water and ethanol, the substrates were further cleaned with UV ozone treatment for 15 min. A 30 nm TiO_2 compact layer was deposited on the FTO glass via spray pyrolysis at 450°C from a precursor solution of titanium diisopropoxide bis(acetylacetonate) in anhydrous ethanol. Subsequently, a mesoporous TiO_2 layer was deposited by spin-coating for 20 s at 4000 rpm with a ramp of 2000 rpm s^{-1}, using 30 nm particle paste (Dyesol 30 NR-D) diluted with ethanol to achieve a 150-200 nm thick layer. After the spin-coating, the substrates were immediately dried at 100°C for 10 min and then sintered again at 450°C for 30 min under dry air flow.

The perovskite films were deposited from a precursor solution containing 1 M formamidinium iodide (FAI), 1.1 M PbI_2 (TCI Chemicals), 0.2 M methylammonium bromide (MABr) and 0.2 M $PbBr_2$ (Alfa Aesar) in anhydrous dimethylformamide:dimethylsulfoxide (DMF:DMSO, 4:1, Acros). The perovskite solution was spin-coated on the FTO glass in a two-step program; first at 1000 for 10 s and then at 4000 rpm for 30 s. During the second step, 100 µL of clorobenzene was poured on the spinning substrate 15 s prior to the end of the program. The substrates were then annealed at 100°C in a nitrogen filled glove box for 1 h.

The HTM solution (70 mM spiro-OMeTAD, 230 mM 4-*tert*-butylpyridine, TBP, and 35 mM lithium bis(trifluoromethanesulfonyl)imide, LiTFSI, in chlorobenzene) was prepared by dissolving first the LiTFSI in acetonitrile (ACN) (520 mg/mL LiTFSI in ACN) and taking a suitable amount of it to the final chlorobenzene solution.

The SWCNT film was transferred on the formamidinium lead iodide-methylammonium lead bromide $(FAPbI_3)_{0.85}(MAPbBr_3)_{0.15}$ perovskite layer by a simple press transfer method from filter paper.[1] After the transfer, the layer was densified by chlorobenzene. Subsequently, another layer of the film was deposited on the already transferred film in order to reach low sheet resistance. After the double-SWCNT film layer deposition, some of the films were

treated by drop-casting 4 µl of Spiro-OMeTAD solution with LiTFSI and TBP in chlorobenzene (see above) on them (SWCNT:Spiro-OMeTAD film). For some of the cells, the second SWCNT layer was densified only with chlorobenzene, to create solar cells where the SWCNT film functions as the sole HTM-CE. The cells were placed on a hotplate at 55 °C for a few minutes, to speed up the solvent evaporation slightly. After that, silver paint (Leitsilber 200N) was added on the edge of the SWCNT film and on the FTO glass edge of the photoelectrode.

SWCNT film characterization

The SWCNT films were characterized by sheet resistance measurement by a four-point probe (Jandel Engineering Ltd. probe and Agilent 34410A multimeter), optical transmittance by a dual beam UV-Vis-NIR spectrophotometer (Lambda 95D, Perkin-Elmer) and Raman spectroscopy with a laser operating at a wavelength of 633 nm (LabRAM, Horiba Jobin Yvon, S.A.S.).

Solar cell characterization

The solar cells were characterized by *I-V* measurements in the solar simulator (Newport, model 91160) equipped with a Keithley 2400 source meter) providing 1000 W/m^2 AM 1.5G illumination intensity, measured by means of a certified reference silicon solar cell (Fraunhofer ISE). Additional characterization was carried out by incident-photon-to-collected-electron (IPCE) measurement by a setup comprising of a Xenon lamp (Spectral Products ASB-XE-175), a monochromator (Spectral Products CM110) and a LabJack U6 data acquisition board. Also the IPCE setup was calibrated with the reference silicon solar cell. Intensity modulated photocurrent spectroscopy[2] was performed using a 625 nm LED driver at different light intensities and a Metrohm Autolab PGSTAT302N potentiostat. A ZEISS Merlin high-resolution scanning electron microscope (HR-SEM) was used to characterize the morphology of the device cross-section.

The *I-V* curves were fitted with a 1-diode model using Labview "IVFIT" program.[3]

References

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