

Materials

All chemicals and reagents were used as received without further purification. Methylammonium iodide (MAI, 99.8% purity), and tris [2-(1*H*-pyrazol-1-yl)-4-*tert*-butylpyridine] cobalt(III) tris [bis (trifluoromethylsulfonyl)imide] (FK209) were obtained from Dyesol Ltd. Spiro-OMeTAD was supplied by Merck Inc. γ -Butyrolactone (GBL, anhydrous, >99.9% purity) was bought from Aladdin Ltd. Other materials, including lead(II) iodide (PbI₂, 99.999% purity), lead(II) chloride (PbCl₂, 99.999% purity), [6, 6]-phenyl-C₆₁-butyric acid methyl ester (PC₆₀BM, >99.9% purity), dimethyl sulfoxide (DMSO, \geq 99.8% purity), toluene (anhydrous, \geq 99.8% purity), chlorobenzene (anhydrous, 99.8% purity), acetonitrile (anhydrous, 99.8% purity), 1-butanol (anhydrous, 99.8% purity), 4-*tert*-butylpyridine (TBP, 96% purity), titanium diisopropoxide bis(acetylacetonate) (75wt% in isopropanol), titanium(IV) chloride (TiCl₄, \geq 98.0% purity), bis(trifluoro-methane)sulfonimide lithium salt (LiTFSI, 96% purity), were purchased from Sigma-Aldrich.

Fabrication and Characterization of Perovskite Solar Cells

F-doped tin oxide glass substrates (FTO, Pilkington, TEC8, 8 Ω /sq) were patterned by etching with Zn powder and 2M HCl diluted in deionized water. The patterned FTO substrates were cleaned sequentially by ultrasonication in detergent, deionized water, acetone and alcohol for 15 min each. After drying with a N₂ stream, a 15 min UV-ozone treatment was used to further clean the substrates. A thin compact TiO₂ layer was deposited following the procedures: A 0.15 M titanium diisopropoxide bis(acetylacetonate) solution in 1-butanol was spin-coated onto FTO substrates at 4000 rpm for 45 s and annealed at 125 °C for 5 min, and the same process was taken twice with 0.3 M titanium diisopropoxide bis(acetylacetonate) solution. The as-prepared films were sintered at 450 °C for 15 min. After cooling down to the room temperature, the coated TiO₂ films were selectively immersed into 40 mM TiCl₄ aqueous solution at 70 °C for 45 min and then heat-treated at 450 °C for 15 min. After that, the samples were transferred into a nitrogen-filled glovebox, and spin-coated with a PC₆₀BM solution (10mg/mL in chlorobenzene) at 6000 rpm for 45 s, followed by heating at 100 °C for 5 min. To make a uniform perovskite layer, a perovskite precursor solution consisting of 1.26 M PbI₂, 0.14 M PbCl₂ and 1.35 M MAI in the co-solvent of DMSO:GBL (3:7 vol. ratio) was stirred at 60 °C for 2 h,[9] and then deposited onto the PC₆₀BM layer at 1000 rpm for 20 s and 4000 rpm for 60 s. It is notable that 320 μ L anhydrous toluene was injected onto the spinning film after 25 s at 4000 rpm. Subsequently, the as-prepared samples were annealed at 100 °C for 15 min with the thickness of perovskite layer about 300 nm. Next, the hole transport material (HTM) was spin-coated on FTO/TiO₂-TiCl₄/PC₆₀BM/CH₃NH₃PbI_{3-x}Cl_x at 1000 rpm for 10 s and 4000 rpm for 45 s using the prepared HTM solution. The HTM solution contained 90 mg spiro-OMeTAD in 1 mL chlorobenzene with 45 μ L LiTFSI/acetonitrile solution (170mg/mL), 10 μ L *t*BP, and 75 μ L Co(III) complex FK209/acetonitrile solution (7.5mM). Before the final thermal evaporation, all the prepared samples were exposed to a controlled environment with a relative humidity of 15 % for 2 hours to facilitate the oxidation of spiro-OMeTAD. After that, the gold electrode of 100 nm was deposited through a shadow mask to create a device area of 0.125 cm².

Device and Material Characterization

All current density – voltage ($J - V$) curves were recorded using a Keithley 2400 source meter unit under simulated AM 1.5G illumination at an intensity of 100 mW/cm² with a XES-70S1 solar simulator. The system was calibrated using an NREL-certified monocrystal Si photodiode detector before device testing. All of the measurements were carried out in air at room temperature without encapsulation. The UV-visible absorption spectra were measured on a Perkin-Elmer Lambda 950 spectrophotometer. Photoluminescence spectra were collected on an Edinburgh Instruments FLS920 spectrofluorometer with the excitation wavelength of 450 nm. Scanning electron microscopy (SEM) images were obtained on a JSM-7800F SEM. Thin film X-ray diffraction (XRD) measurements were

conducted on a Bruker D8 Advance XRD instrument. The surface morphology of TiO₂ was measured by Dimension Icon Atomic force microscopy (AFM).



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