

Supporting Information for

**Graphdiyne Oxide Doped SnO₂ Electron Transport Layer for High
Performance Perovskite Solar Cells**

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Experimental Section

Materials

SnO₂ colloidal solution (15 wt% in water) was purchased from Alfa Aesar. Dimethyl formamide (DMF), Dimethyl sulfoxide (DMSO), Chlorobenzene (CB), Acetonitrile (ACN) were purchased from Sigma-Aldrich. Lead iodide (PbI₂), Formamidinium iodide (FAI), Methylammonium chloride (MACl) and Methylammonium bromide (MABr) were purchased from Xi'an Polymer Light Technology Corporation. Lithium Bis(trifluoromethane) sulfonimide (Li-TFSI), 4- tert- butyl pyridine (TBP), 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro-OMeTAD) were also purchased from Xi'an Polymer Light Technology Corporation.

Synthesis of GDYO Powder

GDY powder (20 mg) was mixed with concentrated HNO₃ (2 mL), H₂SO₄ (6 mL) and KMnO₄ powder (24 mg), and stirred for 24 h at 80°C. And the suspension was centrifuged at 8000 rpm. The resulting precipitate was re-dissolved into water and dialyzed in water. Finally, the solvent was removed to obtain GDYO powder.

Synthesis of SnO₂(GDYO) Composite

GDYO powder was dissolved in water by ultrasonic treatment for one week, then GDYO suspension with a concentration of 4 mg/mL was obtained. SnO₂ precursor solution was prepared by diluting the SnO₂ colloidal solution to 2.667 wt% with water. After that, a certain amount of GDYO dispersion solution was added into the obtained SnO₂ solution, which was sealing stirred for another 3 h to achieve the deposition of SnO₂ nanoparticles onto GDYO substrate. For a better comparison, varying SnO₂(GDYO) composites (the volume ratio is 1%, 2%, 3%) were prepared by regulating the mixing ratio of GDYO and SnO₂ under the same condition.

Solar Cell Fabrication

The pre-patterned indium tin oxide (ITO) coated glass was ultrasonically cleaned using detergent, deionized water, acetone, isopropanol successively. The cleaned ITO substrates were dried under nitrogen flow and then treated in oxygen plasma cleaning to remove carbon residues. Then, the ITO substrate was spin coated with a thin layer of

SnO₂ nanoparticle film and SnO₂(GDYO) film at 3000 rpm for 30 s, and annealed in ambient air at 150 °C for 30 min. After SnO₂ had been cooled down to room temperature, 1.5 mL of PbI₂ solution (DMF:DMSO = 93:7) was spin coated onto SnO₂ at 1500 rpm for 30 s, and then annealed at 70°C for 45 s. Later, the spin-coating procedure was performed at 2000 rpm for 30 s with a ramp-up of 2000 rpm/s. At 6 s before the end of the procedure, about 210 µL of the mixture solution of FAI: MABr: MACl (90 mg:9 mg: 9 mg in 1 mL IPA) was dropped onto the spinning substrate. Then the perovskite layer coated substrate was transferred onto a hotplate and heated at 150°C for 15 min. The hole transport layer was deposited on top of the perovskite layer at 4000 rpm for 30 s using 2,2',7,7'-tetrakis-(*N,N*-dimethoxyphenylamine)-9,9'-Spirobifluorene (Spiro-OMeTAD) solution, which is composed of 72.3 mg Spiro-OMeTAD, 35 µL bis(trifluoromethane) sulfonimide lithium salt (Li-TFSI) solution (260 mg Li-TFSI in 1 mL ACN), 30 µL 4-tertbutylpyridine, and 1 mL CB. Finally, MoO₃ (8 nm in thickness) and Ag (80 nm in thickness) electrode was deposited successively on top of Spiro-OMeTAD layer by thermal evaporation under high vacuum (1×10^{-7} Pa). The active area, as defined by the overlap of Ag and ITO, is 0.06 cm². For thermal and illumination stability tests, the device based on poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA) hole transport layer doped with tris(pentafluorophenyl)borane (TPFB) replacing spiro-OMeTAD was fabricated. The concentration of PTAA was 30mg/ml and the weight ratio of PTAA/TPFB was 10:1. Afterwards, PTAA was deposited on top of the perovskite layer at a spin speed of 2000 rpm/s for 30 s.

Characterization

Current-voltage (*J-V*) curves were measured using a computer-controlled Keithley 2400 sourcemeter under AM 1.5G solar illumination at 100 mW/cm² (1 Sun) from a Newport Oriel So13A solar simulator. Film morphology was observed by scanning electron microscopy (SEM; Hitachi, S-4800) with an acceleration voltage of 5.0 kV. Height profiles of films were observed from atomic force microscopy (AFM; Bruker, ICON-PT). X-ray photoelectron spectroscopy (XPS; VG Scientific, ESCALab-220i-

XL) data were performed on X-ray photoelectron spectrometer with an Al cathode as the X-ray source. The photoluminescence spectra (PL) were measured by a fluorescent spectrophotometer (F-4600, Hitachi Ltd., Tokyo, Japan) with a 150W Xe lamp as an excitation source at room temperature. Time-resolved photoluminescence (TRPL) was characterized by TRPL (EDINBURGH, FLS-980). The energy band structure was evaluated by the ultraviolet photoemission spectroscopy (UPS) (Thermo Scientific, ESCALAB 250Xi). External quantum efficiency (EQE; Newport, 818-UV) measurements were carried out using a Sciencetech SF150 xenon arc lamp and a PTI monochromator, with the monochromatic light intensity calibrated by a Si photodiode. The electrochemical impedance spectroscopy (EIS; Chenhua, CHI-660) measurements were performed on the electrochemical workstation in dark. Raman spectroscopy (Thermo Scientific DXRxi, 532 nm). Photoluminescence images were measured by FluoView FV1000 illuminated with 405 nm royal-blue LED chips.

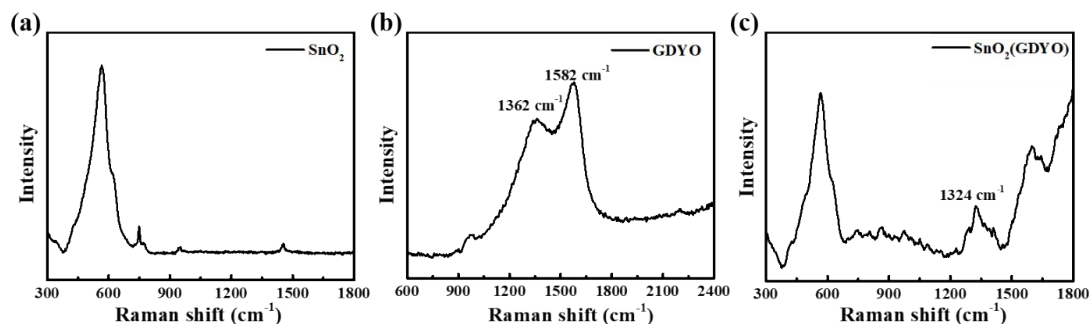


Fig. S1 Raman spectra of (a) SnO_2 , (b) GDYO powder, and (c) $\text{SnO}_2(\text{GDYO})$ powder.

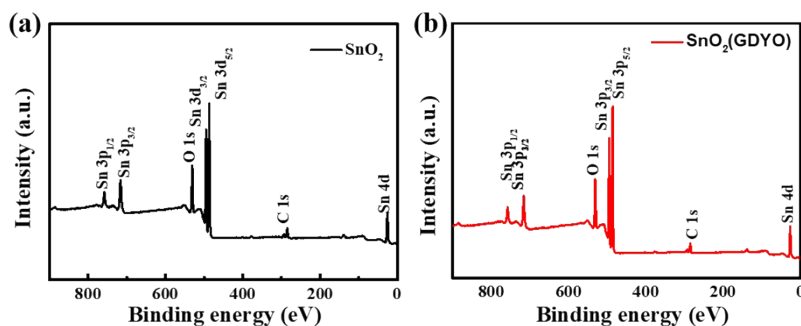


Fig. S2 XPS scans for (a) SnO_2 and (b) $\text{SnO}_2(\text{GDYO})$ ETLs.

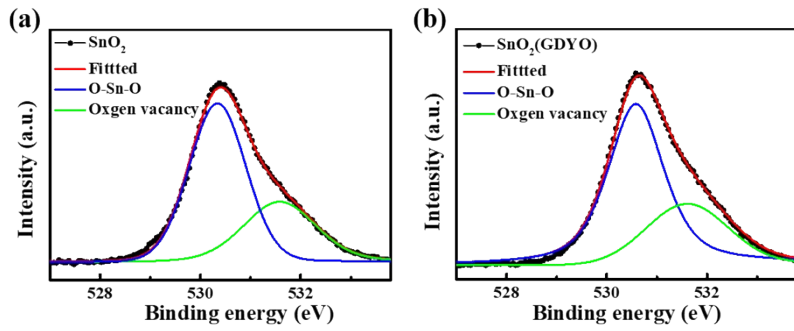


Fig. S3 O 1s peak measured from (a) SnO₂ layer and (b) SnO₂(GDYO) composite layer.

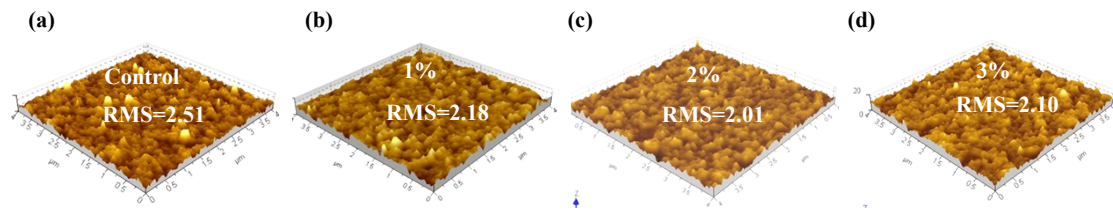


Fig. S4 3D AFM observations for (a) SnO₂, (b) SnO₂(GDYO, 1%), (c) SnO₂(GDYO, 2%), and (d) SnO₂(GDYO, 3%) ETLs.

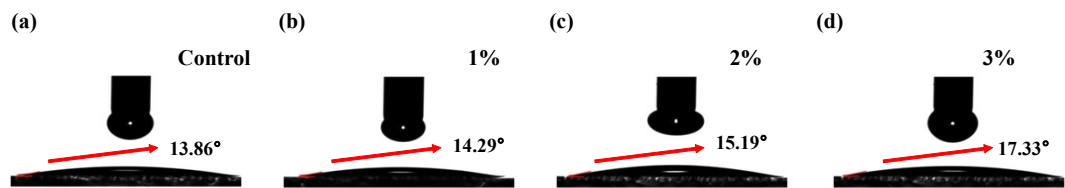


Fig. S5 Images of water droplet contact angles on the surface of (a) SnO₂, and (b-d) SnO₂(GDYO) ETLs with different doping concentrations.

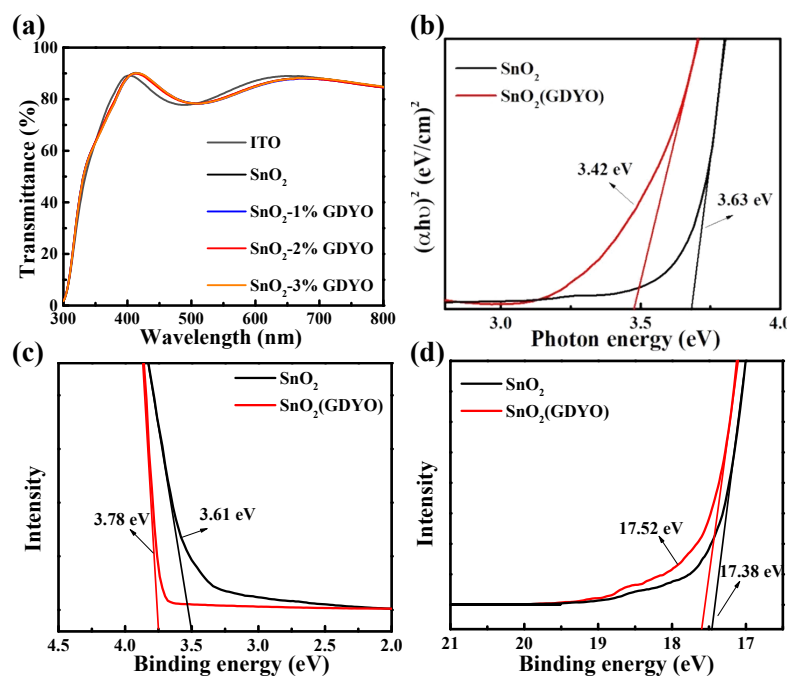


Fig. S6 (a) The transmission spectra of different ETLs measured by UV-Vis spectroscopy. (b) The band gap calculation using the Tauc plot, (c) cut off energy region, and (d) the valence band maximum energy region of pristine SnO₂ and SnO₂ with 2% concentration of GDYO.

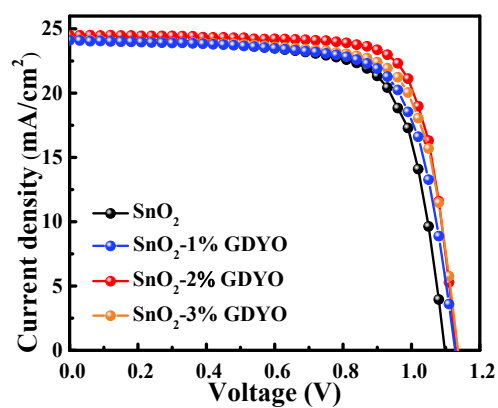


Fig. S7 $J-V$ curves of PSCs based on SnO₂ and SnO₂(GDYO) with different concentrations of GDYO under AM 1.5G simulated illumination.

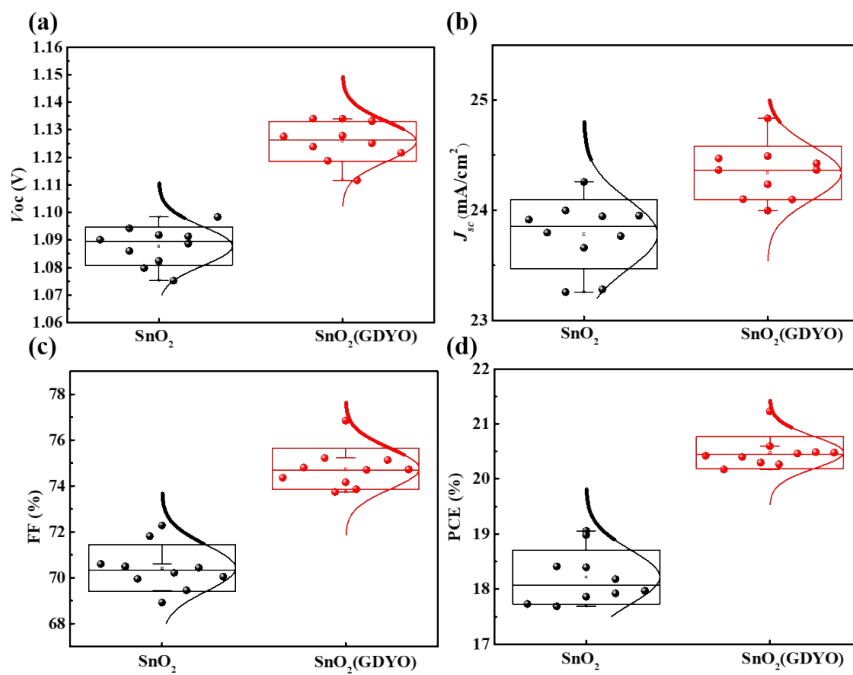


Fig. S8 The standard box plots of the main parameters of 12 devices based on SnO₂ and SnO₂(GDYO) ETLs.

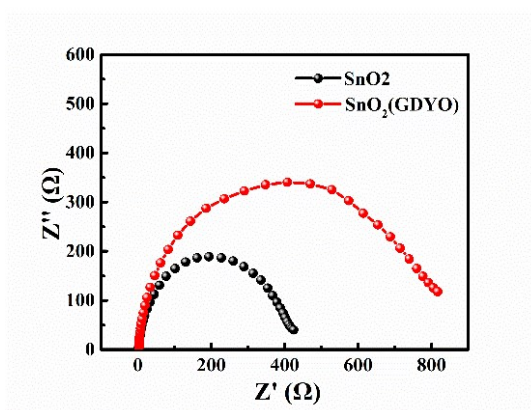


Fig. S9 Impedance spectra of the of devices based on SnO₂ and SnO₂(GDYO) ETLs.

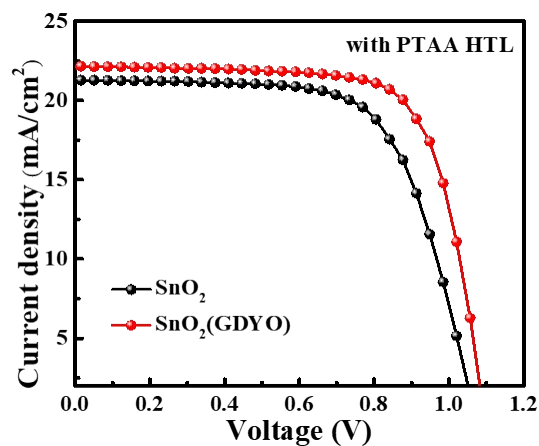


Fig. S10 The initial current density-voltage (J - V) curve for the devices based on SnO_2 ETLs and $\text{SnO}_2(\text{GDYO})$ ETLs with PTAA as hole transport layers (HTLs)

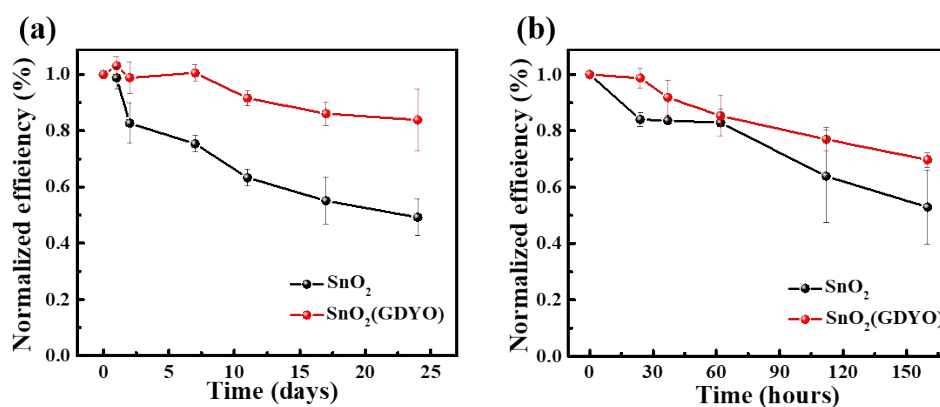


Fig. S11 PCE evolution of SnO_2 and $\text{SnO}_2(\text{GDYO})$ based devices (a) at 80°C heating under the nitrogen atmosphere and (b) under one sun illumination (25°C).