Supporting Information for

**Graphdiyne Oxide Doped SnO$_2$ Electron Transport Layer for High Performance Perovskite Solar Cells**

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Experimental Section

Materials
SnO$_2$ 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 (PbI$_2$), 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 HNO$_3$ (2 mL), H$_2$SO$_4$ (6 mL) and KMnO$_4$ 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 SnO$_2$(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. SnO$_2$ precursor solution was prepared by diluting the SnO$_2$ colloidal solution to 2.667 wt% with water. After that, a certain amount of GDYO dispersion solution was added into the obtained SnO$_2$ solution, which was sealing stirred for another 3 h to achieve the deposition of SnO$_2$ nanoparticles onto GDYO substrate. For a better comparison, varying SnO$_2$(GDYO) composites (the volume ratio is 1%, 2%, 3%) were prepared by regulating the mixing ratio of GDYO and SnO$_2$ 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
SnO$_2$ nanoparticles film and SnO$_2$(GDYO) film at 3000 rpm for 30 s, and annealed in ambient air at 150 °C for 30 min. After SnO$_2$ had been cooled down to room temperature, 1.5 m of PbI$_2$ solution (DMF:DMSO = 93:7) was spin coated onto SnO$_2$ 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-dip-methoxyphenylamine)-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, MoO$_3$ (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 ($1 \times 10^{-7}$ Pa). The active area, as defined by the overlap of Ag and ITO, is 0.06 cm$^2$. 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/cm$^2$ (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) SnO$_2$(GDYO) powder.

Fig. S2 XPS scans for (a) SnO$_2$ and (b) SnO$_2$(GDYO) ETLs.
Fig. S3 O 1s peak measured from (a) SnO$_2$ layer and (b) SnO$_2$(GDYO) composite layer.

Fig. S4 3D AFM observations for (a) SnO$_2$, (b) SnO$_2$(GDYO, 1%), (c) SnO$_2$(GDYO, 2%), and (d) SnO$_2$(GDYO, 3%) ETLs.

Fig. S5 Images of water droplet contact angles on the surface of (a) SnO$_2$, and (b-d) SnO$_2$(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 SnO$_2$ and SnO$_2$ with 2% concentration of GDYO.

Fig. S7 $J$–$V$ curves of PSCs based on SnO$_2$ and SnO$_2$(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 SnO$_2$ and SnO$_2$(GDYO) ETLs.

Fig. S9 Impedance spectra of the devices based on SnO$_2$ and SnO$_2$(GDYO) ETLs.
Fig. S10 The initial current density-voltage ($J-V$) curve for the devices based on SnO$_2$ ETLs and SnO$_2$(GDYO) ETLs with PTAA as hole transport layers (HTLs).

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