

## Supporting Information

Reduced graphene oxide (rGO) grafted zinc stannate ( $\text{Zn}_2\text{SnO}_4$ ) nanofibers scaffolds for highly efficient mixed-halide perovskite solar cells

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## **S1. Experimental Details:**

### ***S1.1 Synthesis of GO:***

The chemical reagents were used without further purification. Graphene oxide (GO) was prepared using modified Hummer's method. In typical reaction 1g of graphite, 1g of NaNO<sub>3</sub> and 23ml of H<sub>2</sub>SO<sub>4</sub> were stirred together in an ice bath. 3g of KMnO<sub>4</sub> was gradually added in the above stirring solution. The suspension was sonicated for 5h to form a thick paste. Then 46ml of ultrapure water was added gradually and stirred for 10 min. Finally, another 140ml of ultrapure water and 10 ml H<sub>2</sub>O<sub>2</sub> (30%) was added into the mixture solution. The above solution was filtered and washed by 5% HCl solution and ultrapure water for several times. The final sediment was dried by vacuum freeze drying to form GO cake. 40mg GO solution was prepared by ultrasonic dissolving the obtained solid in 10ml N,N-dimethylformamide (DMF) solution.<sup>[28]</sup>

### ***S1.2 Preparation of rGO-Zn<sub>2</sub>SnO<sub>4</sub> nanofiber nanocomposite:***

Poly(vinyl pyrrolidone) (PVP, Mw=1,300,000 mol/g), Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (99%+) and Sn(CH<sub>3</sub>COO)<sub>4</sub> (99%+) were purchased from Aldrich. Anhydrous DMF was obtained from J.T Baker. The precursor solution for electrospinning process was prepared by dissolving desired amount of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Sn(CH<sub>3</sub>COO)<sub>4</sub> and PVP in DMF solvent. The homogeneous sol was prepared by overnight stirring at room temperature. The previously prepared GO-DMF solution 0.7ml and 1.5ml was added in Zn<sub>2</sub>SnO<sub>4</sub>-PVP-DMF solution and stirred another 1hr for dispersion of GO-DMF solution (**Figure S1**). The prepared electrospinning solution was carefully sucked into a 10ml glass syringe and fixed horizontally arranged electrospinning equipment. The positive electrode was connected to the needle of the syringe containing precursor solution. The drum rotating speed (400 rpm) and the distance between the needle tip and grounded collector (15 cm) was kept constant. The feeding rate was 0.5mlh<sup>-1</sup> by a syringe pump (KDS-100, KD Scientific). At this point, an electric field potential of 17kV was applied between the needle tip and a grounded collector at a distance of 15 cm. The electro spun GO-Zn<sub>2</sub>SnO<sub>4</sub>/PVP composite nanofibers have been deposited on Al foil. The prepared nanofibers were

further calcined at 700°C for each 1hr in air to remove the organic constituents of the PVP polymer matrix and formation of rGO-Zn<sub>2</sub>SnO<sub>4</sub> scaffold. The prepared sample designated as ZSO, rGO-ZSO<sub>0.7</sub> and rGO-ZSO<sub>1.5</sub> for 0 ml, 0.7ml and 1.5ml GO+DMF solution addition. The thermal annealing temperature was optimized by TGA analysis.<sup>[2]</sup> The crystallinity and composition of the nanofibers were confirmed by XRD, Raman, HRTEM and XPS analysis.

### ***S1.3 Preparation of blocking layer Zn<sub>2</sub>SnO<sub>4</sub> (BI-ZSO)***

Initially, laser pattern F-doped SnO<sub>2</sub> (FTO) substrates (ML20-PL-R, Kortherm Science), were cleaned by sonication in soap, ethanol and isopropanol followed by the plasma treatment before coating the compact layer. The synthesis of BI-ZSO and ZSO fibers were synthesized as per our previous report. The annealed ZSO and rGO-ZSO nanofibers were further used for ZSO paste. The ZSO and rGO-ZSO paste was prepared separately using ethyl cellulose and terpineol solution in ethanol solvent. The prepared ZSO and rGO-ZSO paste was spin coated on BI-ZSO/FTO substrate. The organic solvents were evaporated by annealing process at 500°C for 30min. The prepared ZSO or rGO-ZSO photoelectrodes were further treated with ZnO treatment. For the ZnO treatment, the ZSO and rGO-ZSO photoelectrodes were immersed in a zinc acetate solution (0.05m) in an ethanol bath for 30 min at 50°C. After the films were rinsed with ethanol and air dried and sintered at 500°C for 1 h.

### ***S1.4 Preparation of methylammonium lead iodide (MAPbI<sub>3</sub>):***

Methylammonium lead iodide (MAPbI<sub>3</sub>) was synthesized as per our previous report [1]. In typical experiment, drop wise addition of hydroiodic acid (aqueous, 57 wt %, Sigma-Aldrich) to a solution of methylamine (aqueous, 40 wt %, TCI Chemicals) in an ice bath. The ice-cold solution was stirred for 2 hr, and the solvent was evaporated using a rotary evaporator (95mbar vacuum, 400rpm rotation). The white coloured product was dissolved in ethanol and recrystallize using diethyl ether. Fresh white coloured

crystals were washed three times using diethyl ether and dried in vacuum for 24h. The resulting white solid product was further used for MAPbI<sub>3</sub> synthesis. The MAPbI<sub>3</sub> precursor solution was prepared by dissolving equimolar amounts of MAI and lead iodide (PbI<sub>2</sub>) (Aldrich, 99.999%) in anhydrous  $\gamma$ -butyrolactone (GBL) (40% by weight, Sigma-Aldrich) at 60°C and stirred 12h. The prepared yellow colored solution was filtered by twice using syringe filter (Whatman GD/X PVDF pore size 0.45 $\mu$ m).

### **S1.5 Preparation of methylammonium lead tribromide (MAPbBr<sub>3</sub>)**

Methylammonium lead bromide (MABr) was synthesized by the dropwise addition of hydrobromic acid (HBr) (48 wt% in water, Sigma-Aldrich, St Louis, MO, USA) to a methylamine solution (aqueous, 40 wt%, TCI Chemicals, Tokyo Chemical Industry Co. Ltd., Tokyo, Japan) in an ice bath. The ice-cold solution was stirred for 2 h followed by the solvent evaporation using a rotary evaporator (95mbar vacuum, 400 r.p.m. rotation) at 60 °C. The resulting white product was dissolved in ethanol and recrystallized using diethyl ether. The fresh fine white crystals were washed three times using diethyl ether and then dried in vacuum for 24 h. The resulting white solid product was used for the MAPbBr<sub>3</sub> synthesis. The MAPbBr<sub>3</sub> precursor solution was prepared by dissolving equimolar amounts of MABr and lead bromide (PbBr<sub>2</sub>) (99.999%, Sigma-Aldrich) in DMSO (Alfa Aesar, Ward Hill, MA, USA) at room temperature overnight. The prepared transparent solution was filtered by a syringe filter (Whatman GD/X PVDF pore size 0.45  $\mu$ m).

The clear yellow solution was dripped on top of the ZSO, rGO-ZSO nanofibrous photoelectrode, and the film was soaked for 30sec and then spun at 2500 rpm for 45s and 3500rpm for 45s with one ramp rate. The GBL solvent was evaporated

on a hot plate for 10 min to form crystalline MAPbI<sub>3</sub> film. The MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> perovskite solution was prepared by dissolving the desired amounts of MAI, MABr, lead iodide (PbI<sub>2</sub>) and lead bromide (PbBr<sub>2</sub>) (Aldrich, 99.999%) in anhydrous  $\gamma$ -butyrolactone (GBL) in dimethyl sulfoxide (DMSO) (Sigma-Aldrich) (7:3 v/v) at 60°C overnight.

### **S1.6 Synthesis of the formamidinium lead iodide (FAPbI<sub>3</sub>) perovskite:**

Formamidinium NH<sub>2</sub>CH=NH<sub>2</sub>I (FAI) were first synthesized by reacting 30 ml hydroiodic acid (57% in water, Aldrich) and 15 g formamidine acetate (Aldrich) in a 250 ml round-bottomed flask at 0°C for 2 h with stirring. The precipitates were recovered by evaporating the solutions at 60°C for 2 h. The products were dissolved in ethanol, recrystallized using diethyl ether, and finally dried at 60 °C in a vacuum oven for 24 h. The desired amount of FAI and PbI<sub>2</sub> powder dissolved in GBL/DMSO (7:3 v/v) and stirred overnight at 60°C. The filtered solution used for synthesis of FAPbI<sub>3</sub> thin films. For (FAPbI<sub>3</sub>)<sub>1-x</sub>(MAPbBr<sub>3</sub>)<sub>x</sub> (x=0.15) were synthesized by reacting FAI, MABr, PbI<sub>2</sub> and PbBr<sub>2</sub> powder with desired amount in GBL/DMSO solution. The prepared solution was further stirred overnight at 60C and used for the deposition of (FAPbI<sub>3</sub>)<sub>1-x</sub>(MAPbBr<sub>3</sub>)<sub>x</sub> (x=0.15).

The hole transport material (HTM) was prepared by as per our previous report [1]. The 180 mg 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenyl-amine)-9,9'-spirobifluorene (spiro-MeOTAD, Merck) dissolved in 1mL chlorobenzene (99.8%, Aldrich) with addition of 37.5  $\mu$ L bis(trifluoromethane) sulfonimide lithium salt (LiTFSI, 99.95%, Aldrich) (170mgml<sup>-1</sup>) in acetonitrile and 17.5  $\mu$ L 4-tert-butylpyridine (TBP, 96%, Aldrich). For the poly[bis(4-phenyl)(2,4,6-trimethylphenyl)amine] (PTAA)-based HTM 15mg of PTAA (EM Index, Mw=17 500 gmol<sup>-1</sup>) in toluene (1.5ml) was mixed

with 15  $\mu\text{l}$  LiTFSI (170 mg) in acetonitrile (1ml) and 7.5  $\mu\text{l}$  4-tert-butylpyridine. The prepared spiro-MeOTAD HTM solution was spin-coated on the FTO/Bi-ZSO/rGO-ZSO/MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> substrate at 3,000 r.p.m for 30s. Then the substrates were transferred to a vacuum chamber and evacuated to a pressure of  $2 \times 10^{-6}$  mbar. For the counter electrode, a 80 nm thick Au contacts were deposited on the top of the HTM over layer by a thermal evaporation (growth rate  $\sim 0.5 \text{ \AA/s}$ ). The active area of this electrode was fixed at  $0.03 \text{ cm}^2$ . The active area was calculated as per gold and laser pattern cross-sectional area.

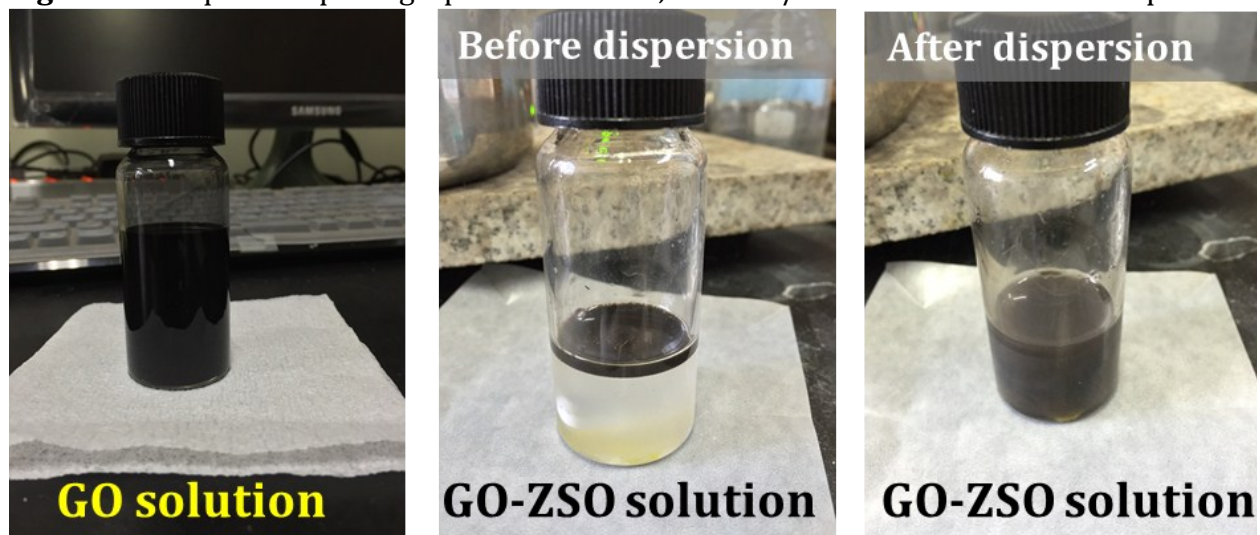
### ***S1 Characterizations***

X-ray diffraction (XRD) measurements were carried out using a X'Pert<sup>3</sup> Powder spectrometer (PANalytical) with CuK $\alpha$  line of  $1.5410 \text{ \AA}$ . The surface morphology of the prepared samples was recorded by a field emission scanning electron microscope (FESEM; S-4700, Hitachi). The elemental information regarding the deposited samples were analyzed using an X-ray photoelectron spectrometer (XPS) (VG Multilab 2000-Thermo Scientific, USA, K-Alpha) with a multi-channel detector, which can endure high photonic energies from 0.1 to 3 keV. Thermal analysis was carried out with a Shimadzu-TGA-50 TG-DTA thermal analyzer in a nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ . The micro-Raman spectra of the ZSO and rGO-ZSO nanofibers was recorded in the spectral range of  $100\text{--}2500 \text{ cm}^{-1}$  using a micro-Raman spectrometer (inVia Reflex UV Raman microscope (Renishaw, U.K.), KBSI, Gwangju-center) that employs a He-Ne laser source with an excitation wavelength 633 nm and resolution of  $1 \text{ cm}^{-1}$  at 15 mW laser power.

The cells were illuminated using a solar simulator at AM 1.5 G for 10 s, where the light intensity was adjusted with an NREL-calibrated Si solar cell with a KG-5 filter to 1 sun

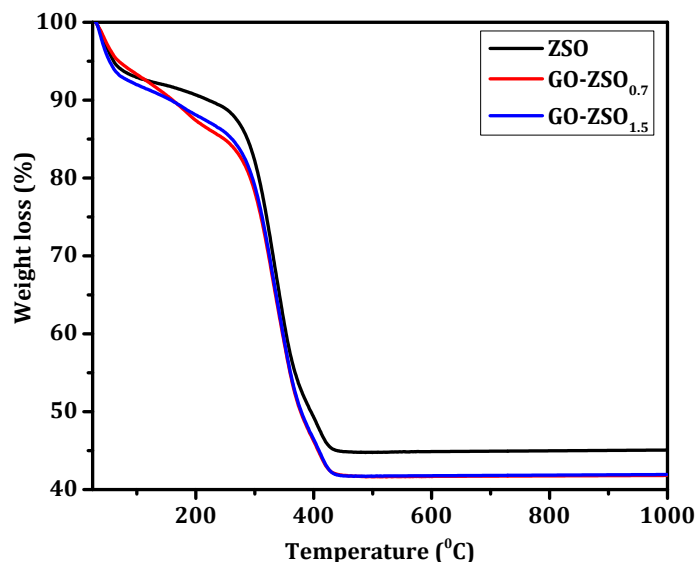
intensity ( $100 \text{ mW cm}^{-2}$ ). The IPCE spectra were measured as a function of wavelength from 300 to 1100 nm on the basis of a Spectral Products DK240 monochromator. Impedance spectroscopy (IS) was conducted using Iviumstat (Ivium Technologies B.V., Eindhoven, the Netherlands) at an open-circuit potential at frequencies ranging from  $10^{-1}$  to  $10^5$  Hz with an AC amplitude of 10 mV. Z-view2.8d (Scribner Associates) was used to fit the IS spectra to the equivalent circuit based on the transmission line model. The DC bias potential was applied in 0.05V step intervals. Time-resolved photoluminescence (PL) decay transients were measured at  $750 \pm 20 \text{ nm}$  using excitation with a 470nm light pulse at a frequency of 5MHz from the Spectrophotometer F-7000.

**Figure S1** Sequential photographs of GO-DMF, GO-ZSO/PVP before and after dispersion.





**Figure S2** TGA curves of  $\text{Zn}_2\text{SnO}_4/\text{PVP}$ ,  $\text{GO-Zn}_2\text{SnO}_{4(0.7)}/\text{PVP}$  and  $\text{GO-Zn}_2\text{SnO}_{4(1.5)}/\text{PVP}$ , composite nanofibers.

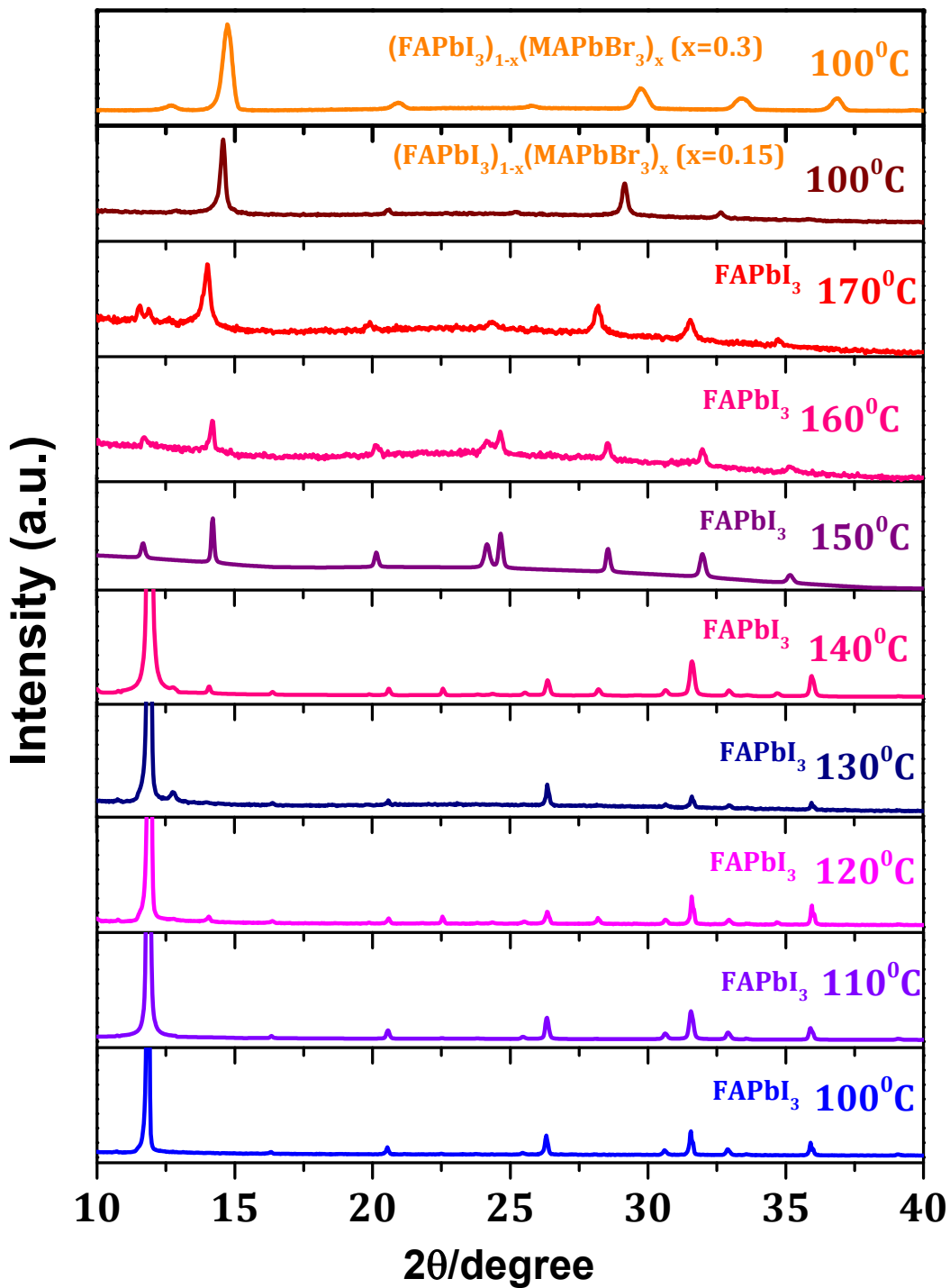


The decomposition temperature of  $\text{ZSO}/\text{PVP}$ ,  $\text{GO-ZSO}_{0.7}/\text{PVP}$  and  $\text{GO-ZSO}_{1.5}/\text{PVP}$  sample was determined by thermogravimetric analysis (TGA). **Figure S2** shows TGA curves of  $\text{ZSO}/\text{PVP}$  and  $\text{GO-ZSO}/\text{PVP}$  nanofibers. All samples showed weight loss began to occur at approximately 350 °C, and was complete at about 480°C. The TGA curve of bare  $\text{Zn}_2\text{SnO}_4/\text{PVP}$  show similar nature is as per previous report.<sup>[1]</sup>

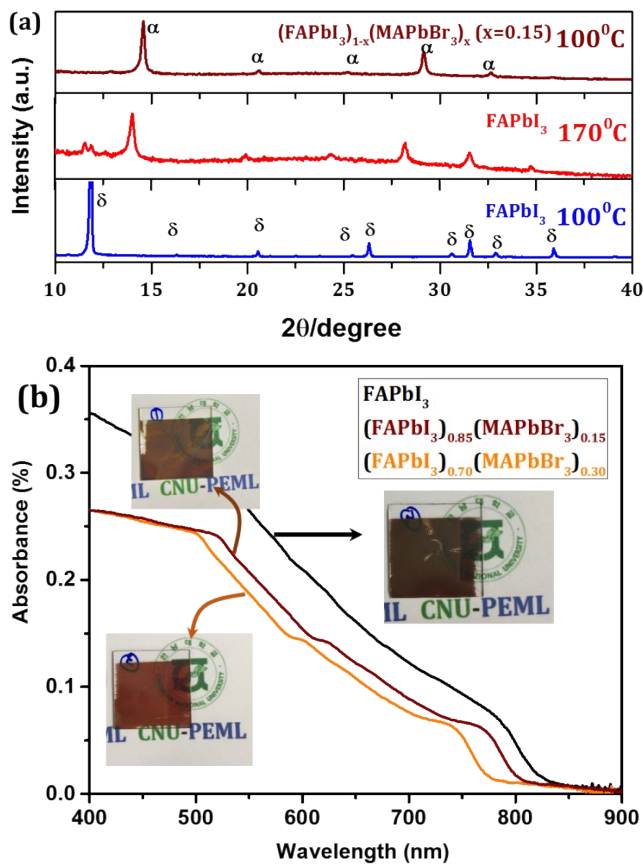
In case of  $\text{GO-Zn}_2\text{SnO}_4/\text{PVP}$  nanofiber sample, the first stage is from room temperature 25°C to 120°C which can be attributed to the dehydration process of water molecules in the interlayer of graphene oxide and loss of chemically bonded oxygen containing functional groups. The second is from 120°C to 250°C, it is due to the burning decomposition of oxygen-containing groups attached to graphene oxide

layers. And the third stage is from 280°C to 450°C which can be assigned to the burning decomposition of carbon skeleton. The total remaining residue mass percentage for ZSO, rGO-ZSO<sub>0.7</sub> and rGO-ZSO<sub>1.7</sub> sample was 44.7748%, 41.6992% and 41.6356% respectively. The loss of mass ratio of bare ZSO scaffold and rGO-ZSO is about 59-57% which is consistent with previous results. The 500 °C annealing temperature is enough for complete decomposition of PVP. However, as per our previous results, the sample annealed at 700°C showed highly porous scaffold. Therefore we have annealed all samples at 700°C. **Figure S2** shows the TGA curves of the ZSO/PVP and GO-ZSO/PVP nanofibers, indicating that the weight loss for GO-ZSO nanofibers are more compared to bare ZSO/PVP nanofibers indicating successful grafting of rGO around the ZSO nanofibers.

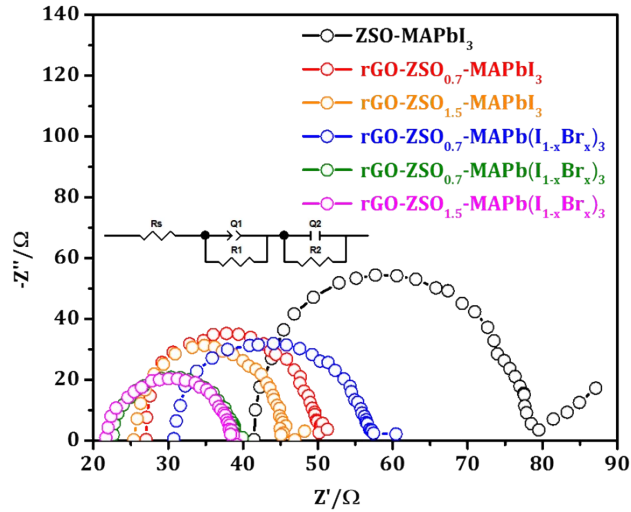
**Figure S3** XRD spectra of FAPbI<sub>3</sub> this films deposited on glass substrate and annealed at different temperature. Annealing time for all sample were 10min on hot plate. The upper XRD patterns show (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> (win colored) (FAPbI<sub>3</sub>)<sub>0.85</sub>(MAPbBr<sub>3</sub>)<sub>0.15</sub> (orange colored) perovskite deposited on glass substrate and annealed at 100°C.



**Figure S4** (a) XRD patterns of the  $\text{FAPbI}_3$  (annealed at  $100^\circ\text{C}$  and  $170^\circ\text{C}$ ) and  $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$  ( $x=0.15$ ) perovskites deposited onto glass substrate (b) UV-Vis optical absorbance spectra of  $\text{FAPbI}_3$  ( $170^\circ\text{C}$ ) and  $(\text{FAPbI}_3)_{1-x}(\text{MAPbBr}_3)_x$  ( $x=0.15, 0.30$ ) deposited on glass substrates.



## Solid state impedance spectroscopy



**Figure S5** Nyquist plots of MAPbI<sub>3</sub> and MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> perovskite solar cells based on ZSO and rGO-ZSO nanofibers. All measurements were recorded in the open circuit state recorded in dark

**Discussion:** The ssIS analyses were performed in the dark on these devices to further understand the role of rGO on ZSO nanofiber in PSCs. **Figure S5** presents the Nyquist plots measured at a voltage bias of 0.9 V. In this Nyquist plot, the semicircle at high frequencies vanishes for all perovskite devices due to the very thin ZSO films has been deposited employed.<sup>[1]</sup> It is also well known that the  $R_{\text{rec}}$  is inversely proportional to the electron recombination rate. Therefore, the simplified circuit model, shown in the inset of **Figure S5**, represents the case in which no transverse line (TL) is observed. In solar cells with perovskite absorbers, the dominant electron loss pathway is the recombination of electrons from the ZSO nanofibers with the holes from the conductor. This recombination lowers the steady state electron density in the ZSO nanofibers film, thus affecting the open-circuit potential of the device. The impedance semi-circle corresponds to the internal

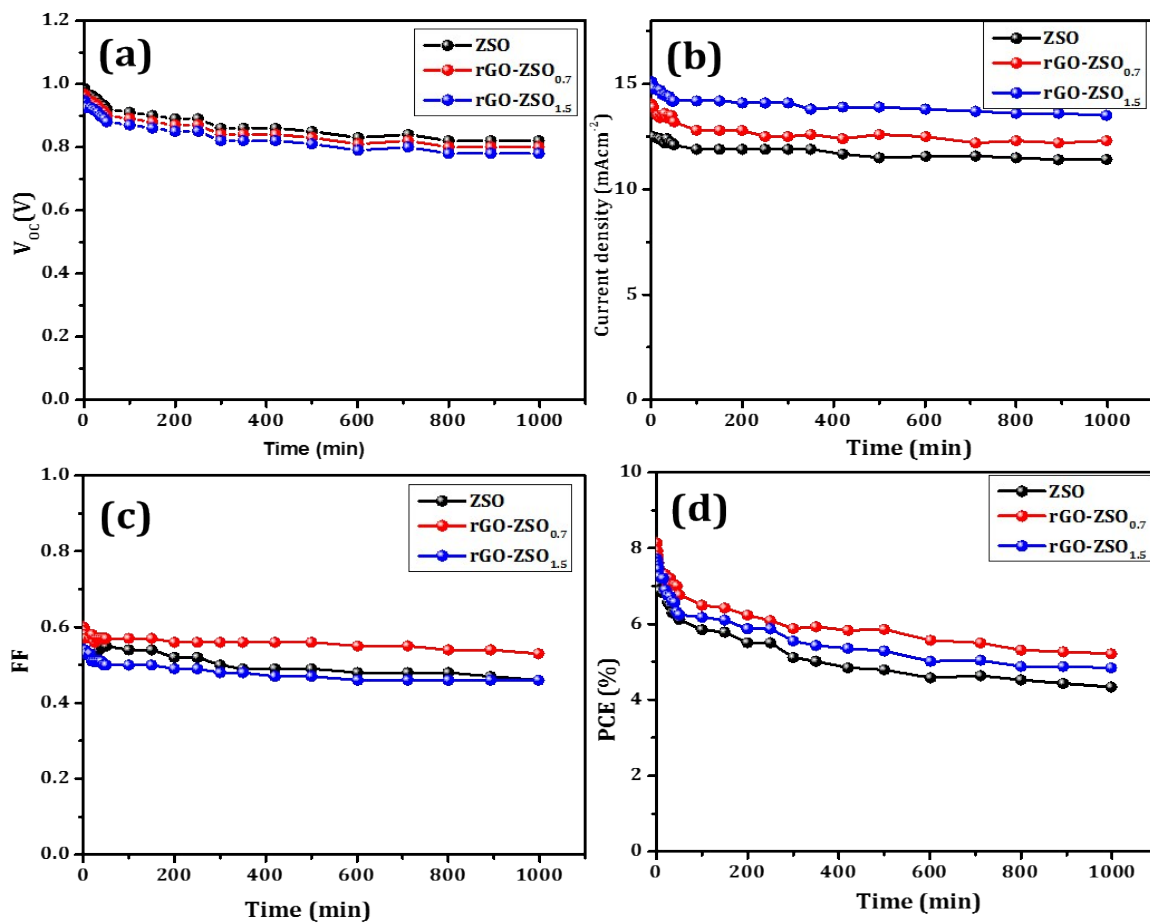
resistance of the interface between the ZSO and the perovskite absorbing layer. The radius of each arc is correlated with the charge transfer ability of the corresponding ETL; the smaller the radius the better the charge transfer ability. The diameter of the semi-circle of the rGO-ZSO<sub>0.7</sub>-MAPbI<sub>3</sub> sample is drastically suppressed than other devices, indicating the slower recombination rate and smaller internal resistance.

However, the diameter is smaller for the rGO-ZSO<sub>0.7</sub>-MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> sample than for both the ZSO-MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> and rGO-ZSO<sub>1.5</sub>-MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> samples. This indicates that the rGO-ZSO<sub>0.7</sub>-MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> possesses superior charge injection characteristics and low internal resistance. This is due to grafting of rGO in to the ZSO scaffolds, this rGO grafting facilitate a fast electron transfer in the ZSO porous scaffold by taking advantage of the 1D graphene sheet and depressing the electron combination. Therefore the rGO grafting in ZSO scaffold improve the PSC performance.

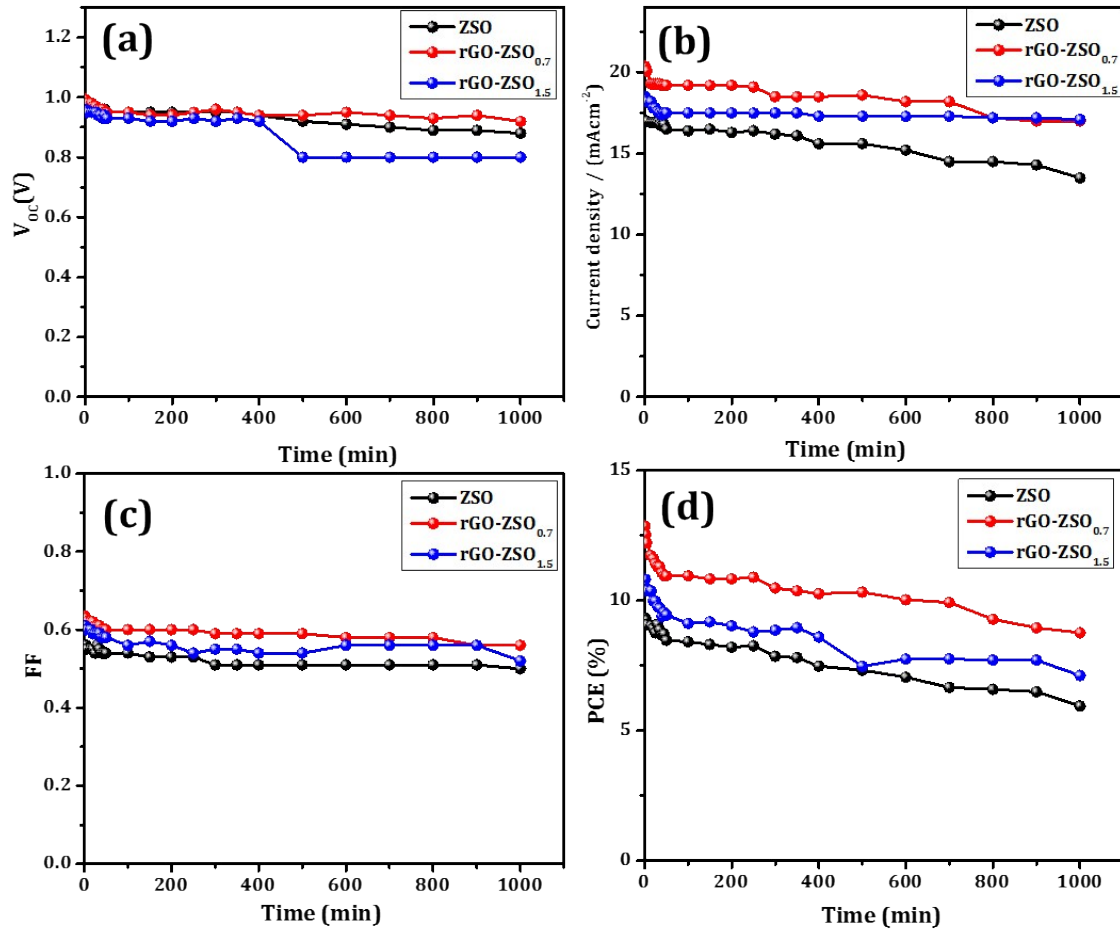
#### **References:**

[1] Kim, H.-S.; Mora-Sero, I.; Gonzalez-Pedro, V.; Fabregat-Santiago, F.; Juarez-Perez, E. J.; Park, N.-G.; Bisquert, J. Nat. Commun. 2013, 4, No. 2242.

**Figure S6** Stability measurements for MAPbI<sub>3</sub> perovskite and ZSO, rGO-ZSO<sub>0.7</sub> and rGO-ZSO<sub>1.5</sub> based ETL.

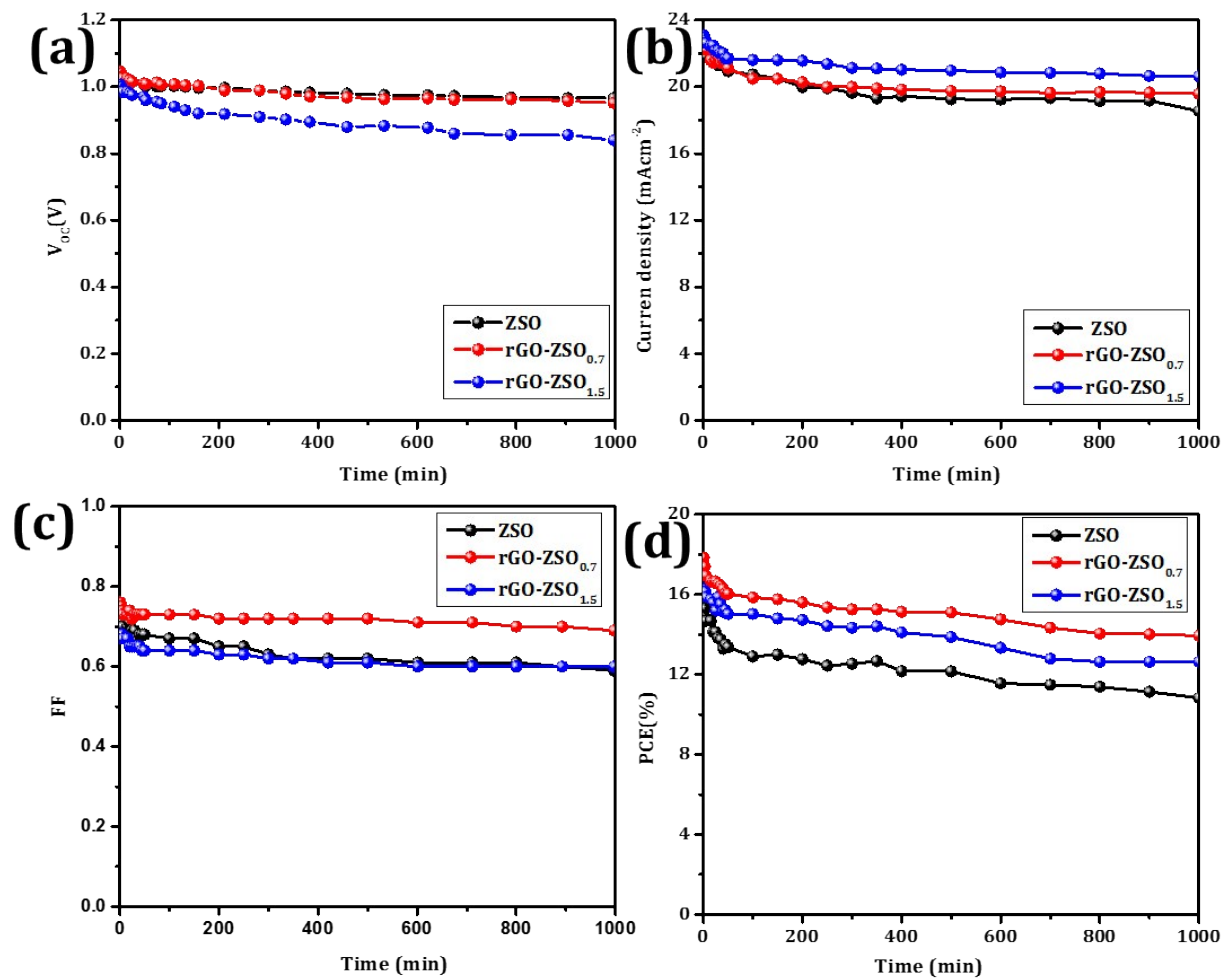


**Figure S7** Stability measurements for MAPb(I<sub>1-x</sub>Br<sub>x</sub>)<sub>3</sub> perovskite and ZSO, rGO-ZSO<sub>0.7</sub> and rGO-ZSO<sub>1.5</sub> based ETL.





**Figure S8** Stability measurements for  $(\text{FAPbP}_3)_{0.85}(\text{MAPbBr}_3)_{0.15}$  perovskite and ZSO, rGO-ZSO<sub>0.7</sub> and rGO-ZSO<sub>1.5</sub> based ETL.



**Figure S9** Histograms of average efficiencies of rGO-ZSO<sub>0.7</sub> ETL and mixed halide perovskites

