Slot-die coating of electron transport layers for perovskite solar cells using water and butanol-based tin oxide dispersions

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SUPPORTING INFORMATION

Experimental Section

Materials

Lead (II) Iodide (PbI2, 99.99%, trace metals basis) was purchased from TCI chemicals. Methyl ammonium iodide (MAI) was purchased from Great cell solar, N, N-dimethylformamide (DMF, anhydrous, 99.8%), dimethyl sulfoxide (DMSO, anhydrous, 99.8%), chlorobenzene (anhydrous, 99.8%), 4-tert-butylpyridine (TBP, 96%), acetonitrile (anhydrous, 99.8%), chlorobenzene (anhydrous, 99.8%) were purchased from Sigma-Aldrich. SnO_2 aqueous colloidal dispersion (15 wt % in H_2O) was purchased from Alfa Aesar. Tin (IV) oxide nanoparticle ink was purchased from Avantama (Avantama N-30, 2.5wt%). Spiro-MeOTAD was purchased from Borun Chemicals. All chemicals are used as received without further purification.

Device fabrication

Solar Cell Preparation: ITO-coated glass substrates (ITO-15 from Optical Filters, UK; size 28 x 24 mm^2) were etched with Zn powder and 2 M HCl to chemically remove the conducting layer from one side of the substrate. After, substrates were cleaned in an ultrasonic bath, starting with 2% RBS 50 (Sigma Aldrich) followed by deionized water, acetone and ethanol for 30 min each. Cleaned substrates were placed on slot-die coater at temperature 80 °C. (No UV-ozone treatment was required) The aqueous SnO_2 nanoparticle solution was diluted by deionized water (DI) in the ratio 1 to 6.5 mL (W-SnO_2). The 2.5 wt % SnO_2 nanoparticle in butanol was diluted to 1 wt% (B-SnO_2).

Slot-die coating: The slot-die coater unit (Compact sheet coater, FOM technologies, Denmark) was placed in a fume hood. The slot-die head is stationary and substrates are moving underneath with a speed of 80 cm/min to deposit W-SnO_2. The pump rate was 90 µl/min, the slot width 2.8 cm and the shim gap was set to 80 µm.

To deposit B-SnO_2, the speed of the hotplate was set to 60 cm/min, pump rate to 200 µl/min and shim gap to 80 µm.

After coating, substrates were immediately placed on a hotplate heated at 140 °C for 30 min. Just before perovskite deposition by spincoating, substrates were subjected to 20 minutes of UV-ozone treatment.

To prepare 1.2 M perovskite solution, methylammonium lead iodide ($MAPbI_3$) precursor solutions were made from an equimolar mixture of MAI (286 mg) and PbI_2 (830 mg) in dimethylformamide (DMF)/dimethyl sulfoxide (DMSO) (4:1 by volume). The perovskite solution was spin coated on slot-die coated SnO_2/ITO film, using 4000 rpm for 20s. During the spinning time between 7 and 10s, 150µL of chlorobenzene was dripped at the center of the substrate.

A 70 mM spiro-OMeTAD (Spiro) solution in chlorobenzene with additives such as 4-tert-butyl pyridine (TBP), 1.8 M Li-TFSI in acetonitrile and 0.25 M FK209 in acetonitrile1 was deposited by spin coating at 2500 rpm for 30 s. The molar ratio of Spiro: TBP: Li-TFSI: FK209 was 1: 3.3: 0.5: 0.05.1

Finally, 80 nm thick gold contact was evaporated on the spiro surface.

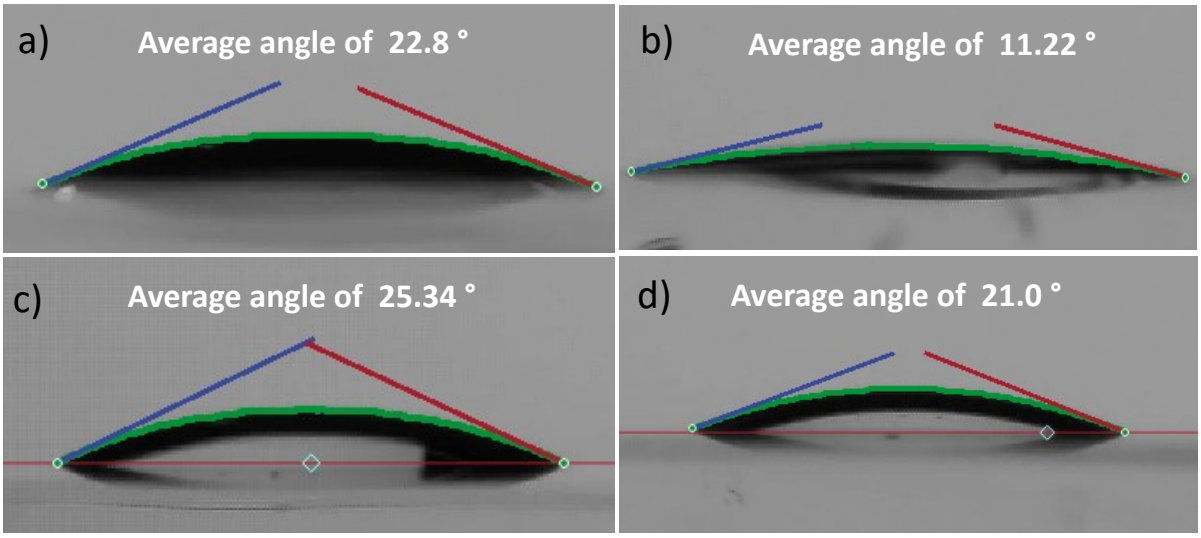

Figure S1: Contact angle of a) W-SnO_2 on ITO without prior cleaning b) After cleaning with DI water c) B-SnO2 on ITO without prior cleaning d) After cleaning with DI water.

Figure S2: SEM cross-section images of perovskite layer on a) B-SnO_2 b) W-SnO_2

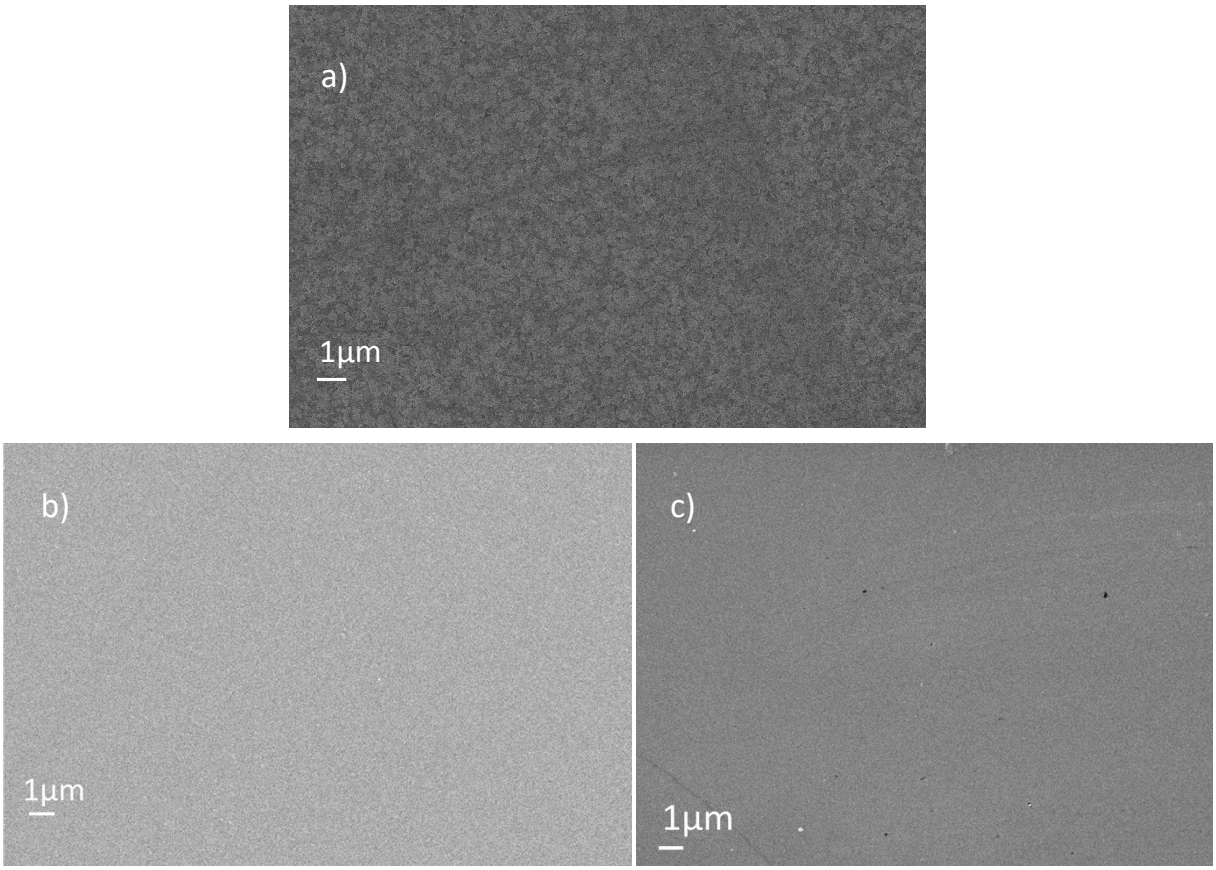

Figure S3: Scanning electron microscopy -top view images a) ITO substrate; b) B-SnO_2 on ITO ;C) W-SnO_2 on ITO.

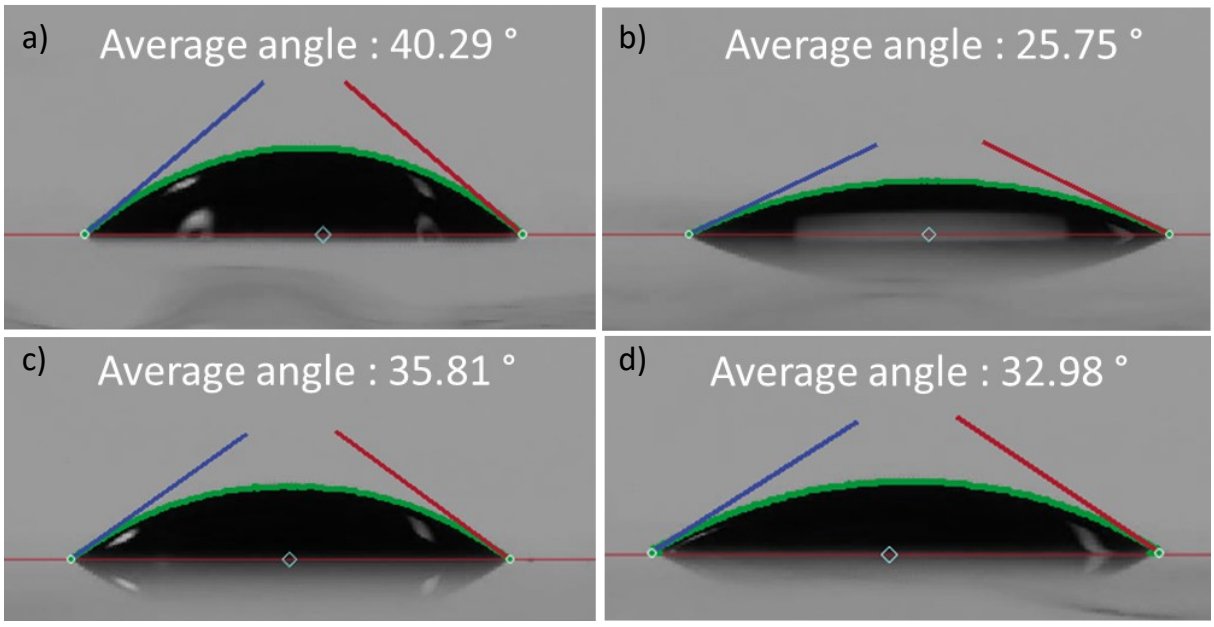

Figure S4: Contact angle of perovskite solution on a) W-SnO_2 without UV-ozone treatment b) W-SnO_2 with UV-ozone treatment c) B-SnO_2 without UV-ozone treatment d) B-SnO_2 with UV-ozone treatment

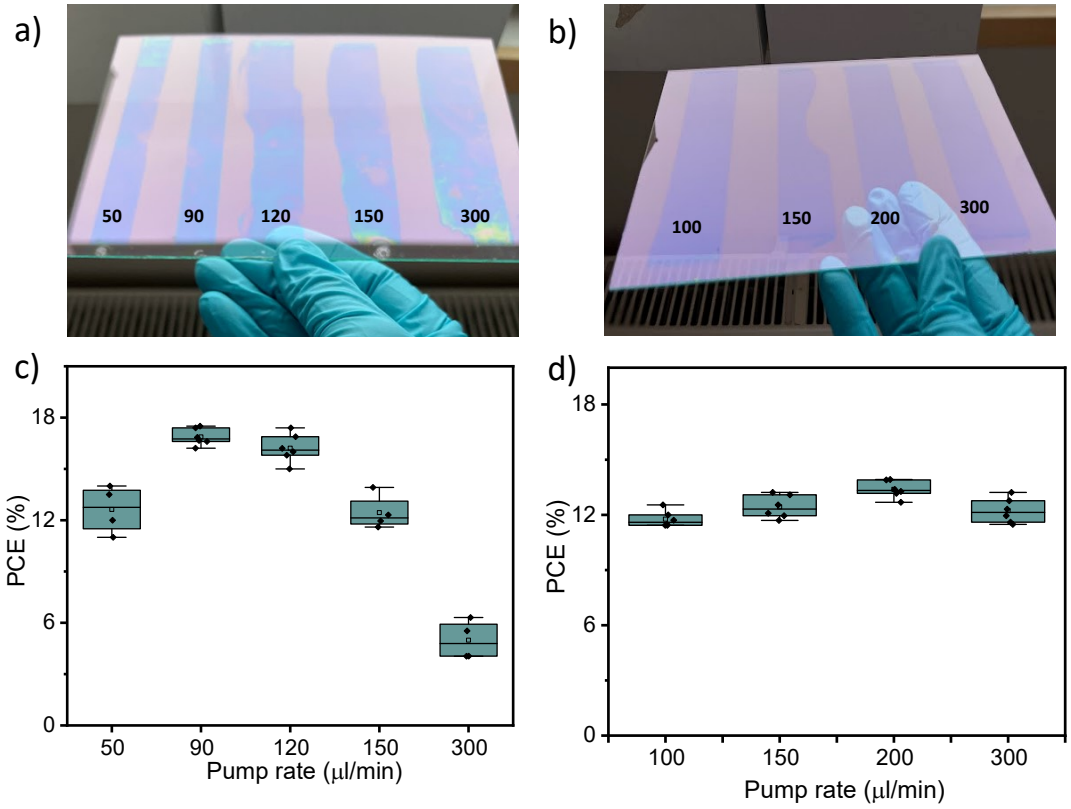

Figure S5: Images of slot die coated SnO_2 a) W-SnO_2 b) B-SnO_2 Corresponding power conversion efficiency v/s pump rate graph c) W-SnO_2 based cell d) B-SnO_2 based cell

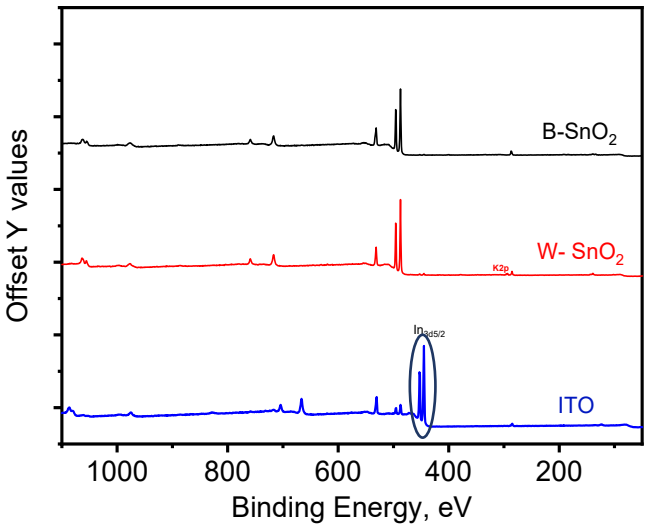

Figure S6: X-Ray Photoelectron spectroscopy of SnO_2 in comparison with bare ITO.

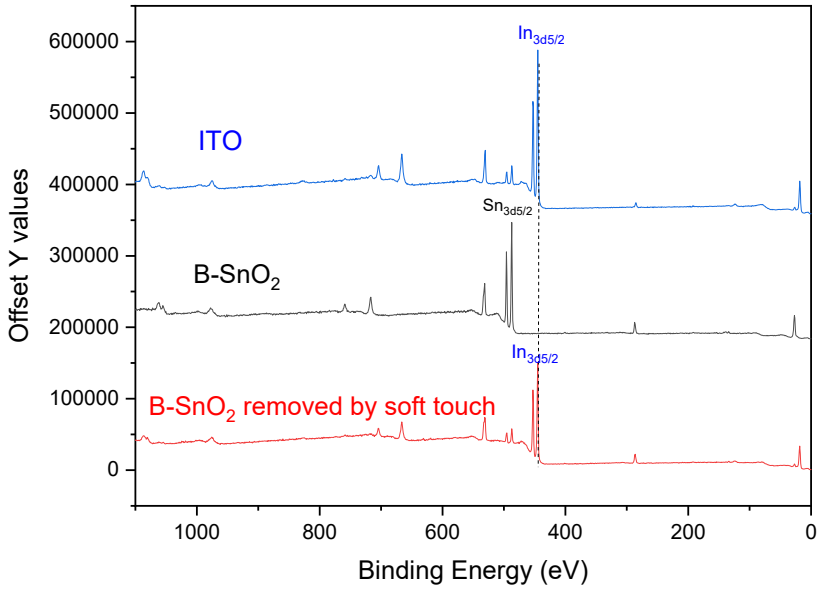

Figure S7: X-Ray Photoelectron spectroscopy of B-SnO_2 before and after soft touch

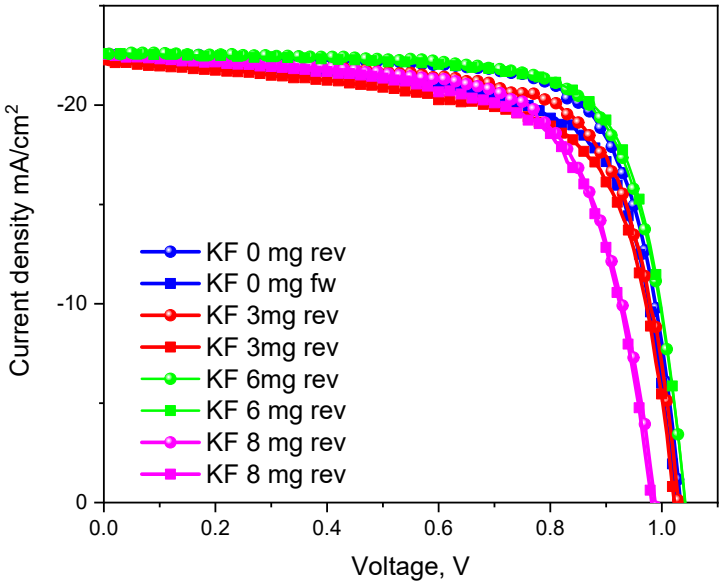

Figure S8: Best JV curves for different amounts of KF addition to SnO2 dispersion.

Table S1 Parameters extracted from best JV Curves (Figure S8)

Name	Voc (V)	Jsc (mA/cm^2)	FF%	PCE %
KF (0)R	1.03	-22.53	73.6	**17.1**
KF (0)F	1.02	-22.55	69.0	**15.9**
KF (3 mg)R	1.02	-22.25	71.1	**16.3**
KF (3 mg)F	1.02	-22.24	67.4	**15.3**
KF (6 mg)R	1.04	-22.5	74.6	**17.5**
KF (6 mg)F	1.04	-22.5	74	**17.4**
KF (8 mg)R	0.99	-22.60	68.2	**15.2**
KF (8 mg)F	0.98	-22.55	67.1	**14.8**

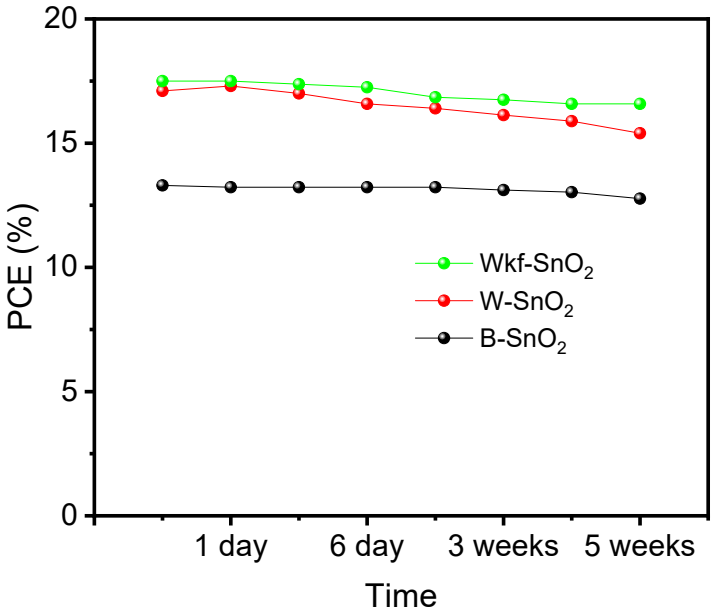

Figure S9: Stability of solar cells over several weeks. Conditions: storage in dry nitrogen atmosphere (< 10% RH) in the dark.

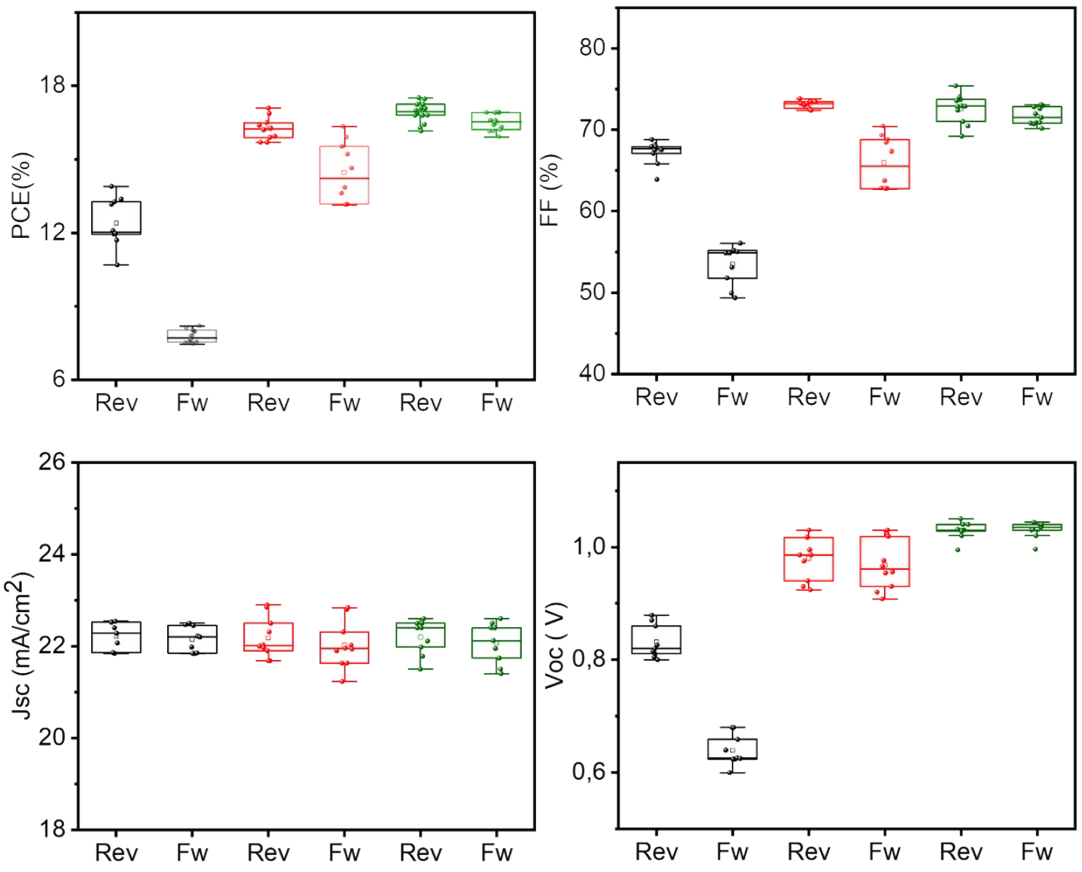

Figure S10: Statistical distribution of solar cell parameters (PCE, FF, Jsc and Voc) B-SnO_2 (Black), W-SnO_2(Red), WKF-SnO_2(Green)

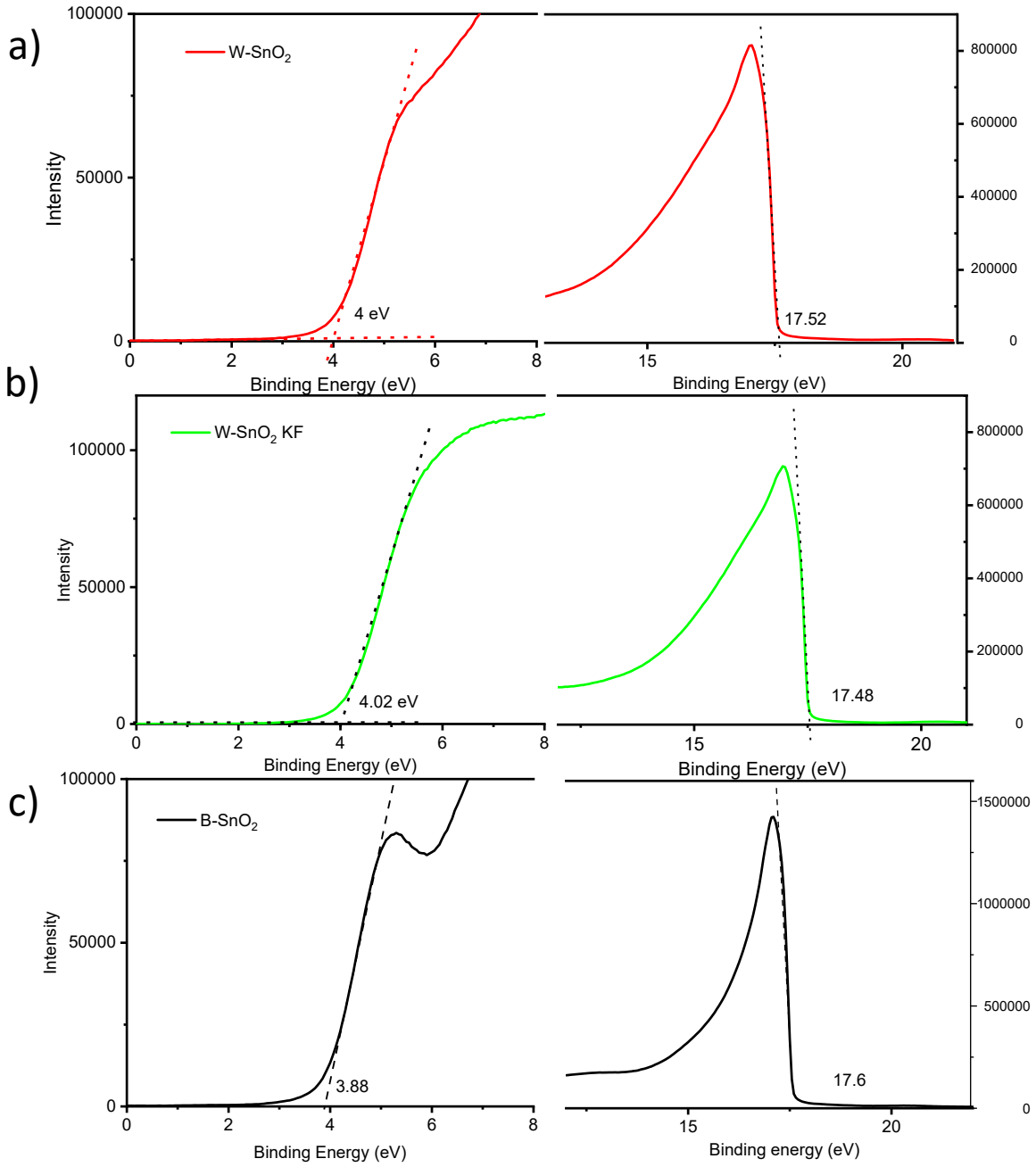

Fig. S11 UPS spectra of valence band region (left) and secondary electron cutoff region (right) (a) W-SnO_2, (b) W-SnO_2-KF (c) B-SnO_2 energy.

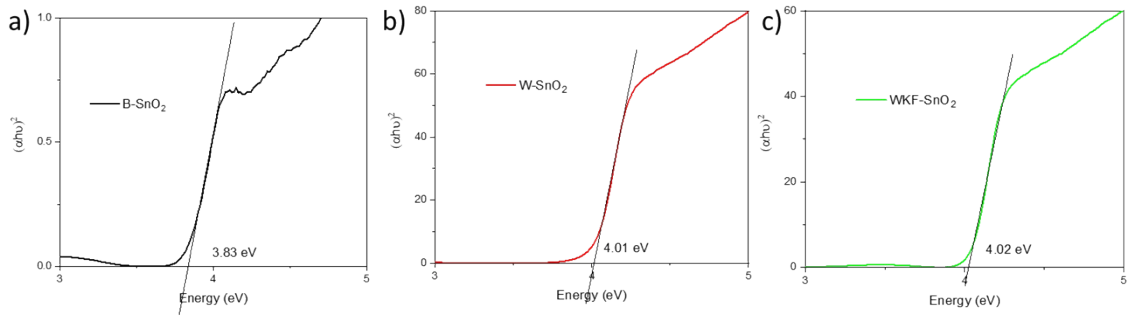

Fig. S12 Tauc plot a) B-SnO_2 b) W-SnO_2 c) WKF-SnO_2

Table S2: UPS parameters for SnO_2 films

Sample	Ecutoff (eV)	Work function (Φ)	E_{VB} (eV)	VBM (eV)	Eg (eV)	CBM (eV)
B-SnO_2	17.60	3.62	3.88	7.50	3.83	3.67
W-SnO_2	17.52	3.70	4.04	7.74	4.01	3.73
W-SnO_2 KF	17.48	3.74	4.08	7.82	4.02	3.81

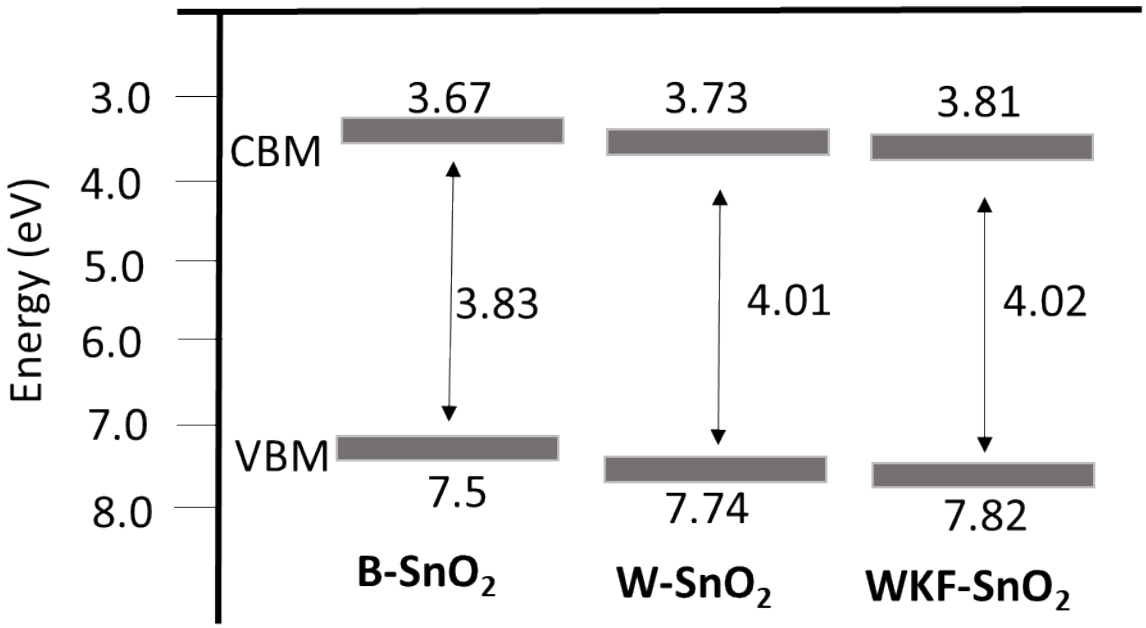

Fig S13: Energy diagram respect to the vacuum energy (E_{vac}) summarizing the energy level extracted UPS spectra, optical bandgap (E_g) (by UV-vis spectroscopy)

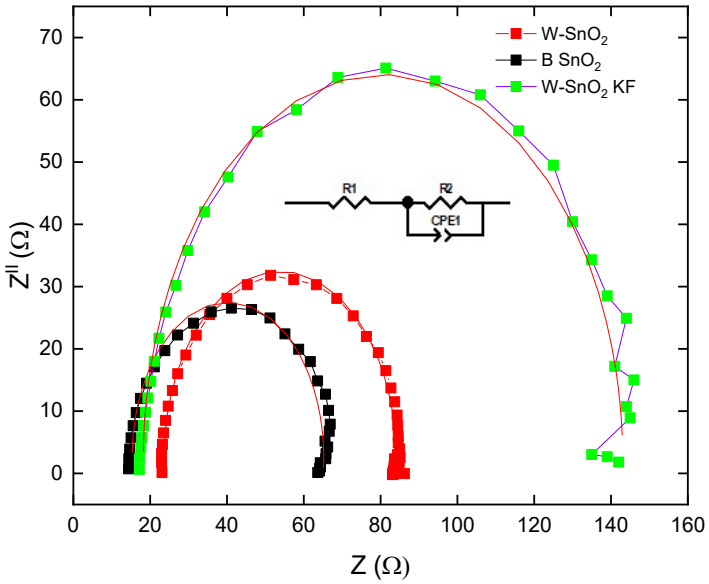

Fig. S14 Nyquist plot of SnO_2 measured at 0.80 V under the dark

Table S3. Series resistance and recombination resistance of Solar cells

Sample	Rs(Ω)	R_{rec}(Ω)
WKF-SnO_2	18.2	124.8
W-SnO_2	**23.6**	**60.3**
B-SnO_2	15.4	49.6