Large-scale Flexible and Highly Conductive Carbon Transparent Electrodes via Roll-to-roll Process and Its High Performance Lab-scale ITO-free PSCs

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Table S1. Electrical properties of PEDOT:PSS films with different CNTs concentration.

Electrode (2000 rpm Spin speed)	Sheet resistance (Ω sq^{-1})	Average Conductivity ($S\ cm^{-1}$)
PEDOT:PSS PH1000	136.83±5.22(131.61)[b]	966.58
PEDOT:PSS PH1000:0.1%CNTs	82.99±5.18(77.81)[b]	1600.48
PEDOT:PSS PH1000:0.3%CNTs	50.01±4.74(45.27)[b]	2674.82
PEDOT:PSS PH1000:0.5%CNTs	40.51±4.75(35.76)[b]	3264.27
PEDOT:PSS PH1000:0.7%CNTs	47.88±4.81(43.07)[b]	2937.69
PEDOT:PSS PH1000:1.0%CNTs	108.71±6.13(114.84)[b]	1230.47

[a] the Sheet resistance was tested by using a four point probe setup with a source measurement unit (Keithley 2400). [b] the best sheet resistance. And the conductivity values were calculated by the equation:

$$\sigma=1/(D\times R)$$

Which σ is conductivity, D is the thickness of film and R is Sheet resistance.

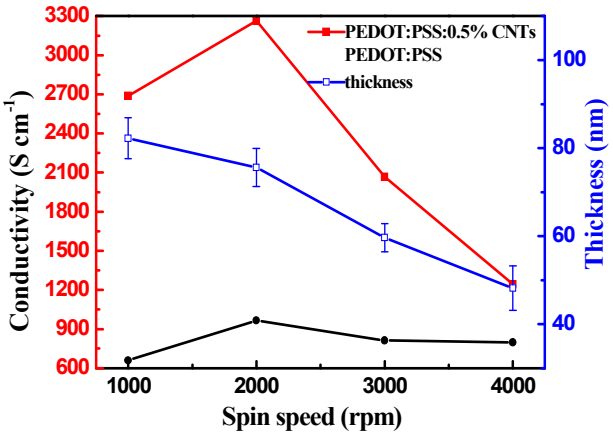

Figure S1 Conductivities of PEDOT:PSS:0.5%CNTs films prepared by spin-coating at different speeds.

Table S2. Electrical properties of PEDOT:PSS and PEDOT:PSS:0.5% CNTs films prepared by spin-coating at different spin-coating speeds.

Electrode	Spin speed(rpm)	Sheet resistance (Ω sq^{-1})	Average Conductivity (S cm^{-1})
PEDOT:PSS PH1000	1000	184.10±11.69(172.41)[b]	660.55
	2000	136.83±5.22(131.61)[b]	966.58
	3000	206.10±10.87(195.23)[b]	813.16
	4000	259.74±10.24(249.50)[b]	798.93
PEDOT:PSS PH1000:CNTs	1000	45.36±5.43(39.93)[b]	2688.41
	2000	40.51±4.75(35.76)[b]	3264.27
	3000	62.57±5.01(57.56)[b]	2678.89
	4000	166.89±7.88(159.01)[b]	1243.43

[a] the Sheet resistance was tested by using a four point probe setup with a source measurement unit (Keithley 2400). [b] the best sheet resistance

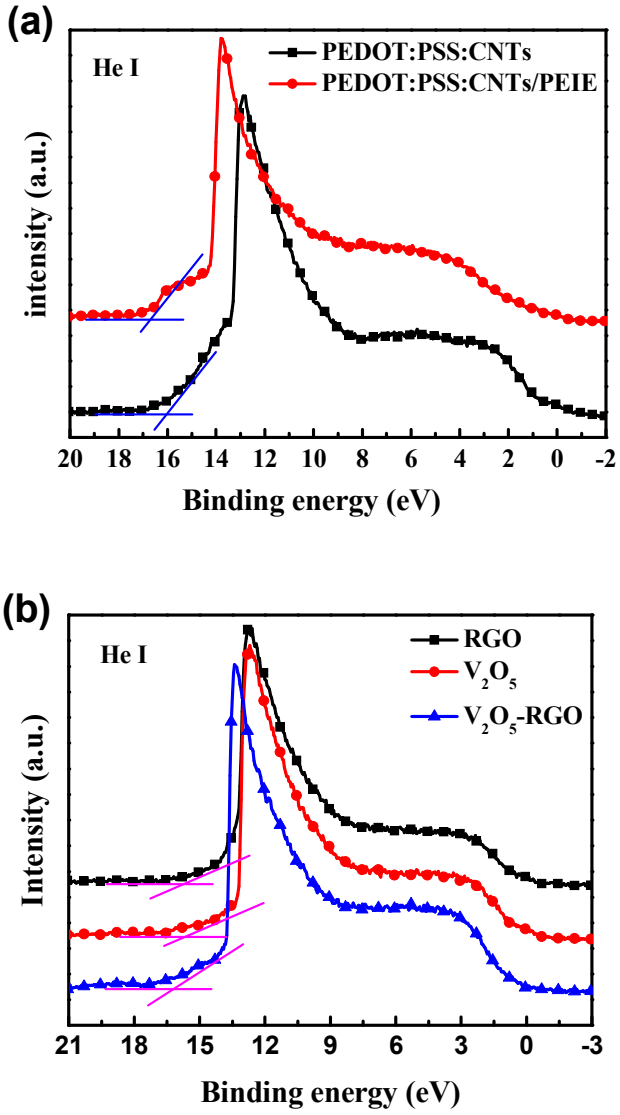

Figure S2. (a) The ultraviolet photoelectron spectroscopy (UPS) of PEDOT:PSS:CNTs and PEDOT:PSS:CNTs/PEIE films, (b) UPS of GO, V_2O_5 and V_2O_5-GO films.

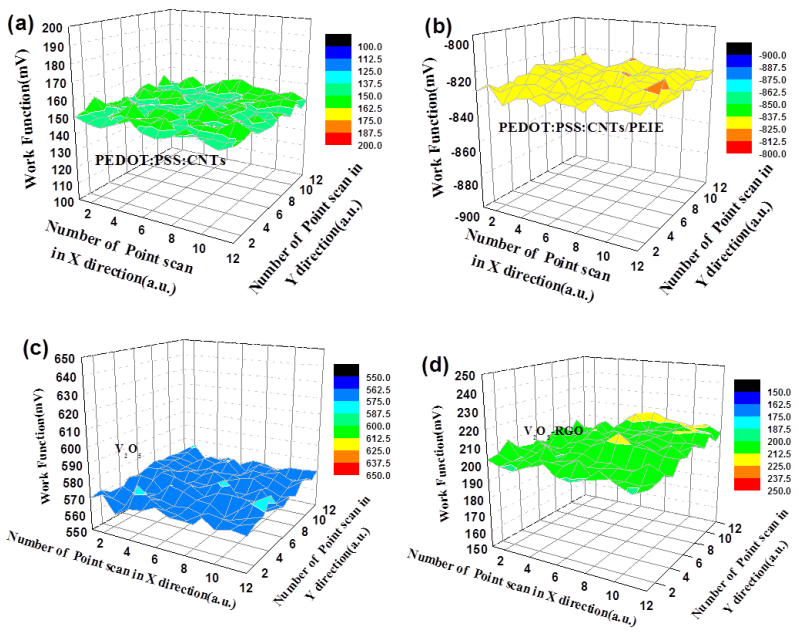

Figure S3. Work function (a) PEDOT:PSS:CNTs, (b) PEDOT:PSS:CNTs/PEIE, (c)V_2O_5, (d)V_2O_5-GO measured by Kelvin probe method

The work functions of the modified cathode were investigated using a Kelvin probe (KP 6500 Digital Kelvin probe, McAllister Technical Services. Co., Ltd.). The samples were measured in a conditioned chamber where the O_2 level is < 25 ppm. The electronic work functions gap between the samples and standard gold probe shown in **Figure S3.** The actual work function of the samples can be obtained through the equation:

$$WF = WF_0 + \Delta WF$$

Where WF is the sample work function, WF_0 is standard gold probe work function (5.1 ev), and ΔWF is the work function gap between samples and standard gold.

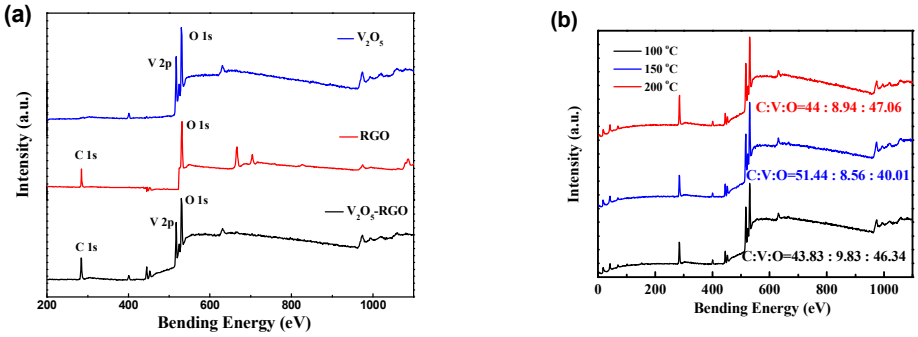

Figure S4. (a) XPS spectrum of V_2O_5, RGO and V_2O_5-RGO films, (b) Determination of the C-V-O ratios of different annealing temperature HTLs by XPS spectra.

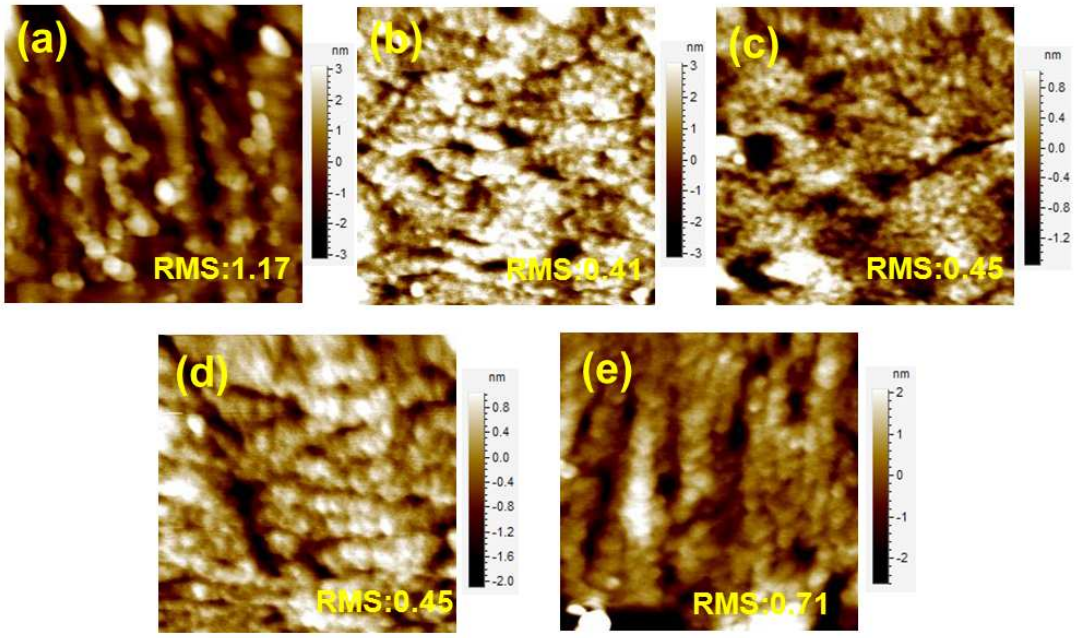

Figure S5. Tapping-mode atomic force microscopy (AFM) images of (a) Reduced Grapheme Oxide (RGO) height image, (b) V_2O_5-RGO with 150 ^oC height image, (c) V_2O_5 height image, (d) V_2O_5-RGO with 100 ^oC height image, (e) V_2O_5-RGO with 200 ^oC height image, (scan range:3μm×3μm).

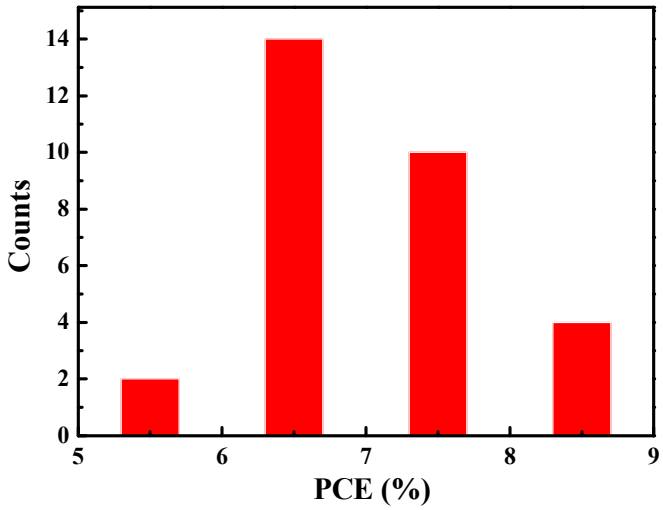

Figure S6 Histogram of solar cell efficiencies for 30 devices F (Glass/PEDOT:PSS:0.5%CNTs/PEIE/ZnO/Glass/PBDTTT-C-T:$PC_{71}BM$/V_2O_5-GO (150 ^oC)/Ag).

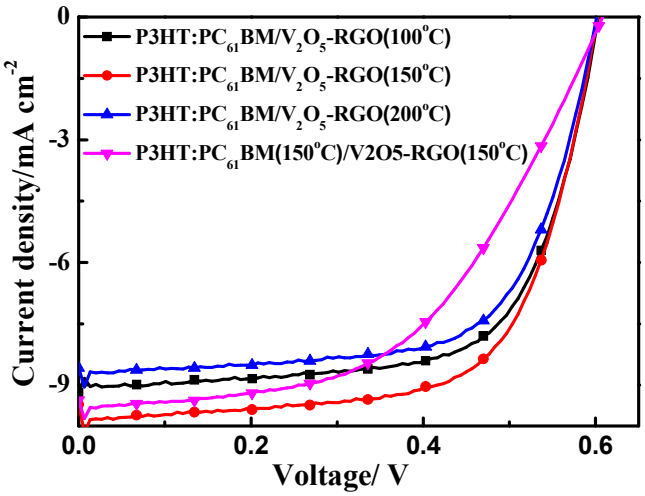

Figure S7. Current (*J*)–voltage (*V*) characteristics of cells based on different annealing conditions.

Table S3. Performance of PSCs with optimized devices under the illumination of AM1.5G, 100 mW/cm^2.

Device	J_{sc} (mAcm^{-2})	V_{oc} (V)	*FF* (%)	PCE (%)
Glass/PEDOT:PSS:0.5%CNTs/PEIE/ZnO/P3HT:$PC_{61}BM$/	9.19	0.60	66.37	3.68
V_2O_5-RGO(100 °C)/Ag	±0.50	±0.02	±1.72	±0.29(3.97)[a]
Glass/PEDOT:PSS:0.5%CNTs/PEIE/ZnO/P3HT:$PC_{61}BM$/	9.48	0.60	68.81	3.94
V_2O_5-RGO (150 °C)/Ag	±0.57	±0.02	±1.83	±0.34(4.28)[a]
Glass/PEDOT:PSS:0.5%CNTs/PEIE/ZnO/P3HT:$PC_{61}BM$/	8.58	0.60	67.32	3.49
V_2O_5-GO (200 °C)/Ag	±0.48	±0.02	±1.94	±0.33(3.82)[a]
Glass/PEDOT:PSS:0.5%CNTs/PEIE/ZnO/P3HT:$PC_{61}BM$	9.36	0.61	52.71	3.01
(150 °C)/V_2O_5-RGO (150 °C)/Ag	±0.48	±0.01	±2.28	±0.25(3.26)[a]

[*]All values represent averages from twelve 19.7 mm^2 devices on a single chip, and the areas were tested with an aperture. [a] best device PCE.

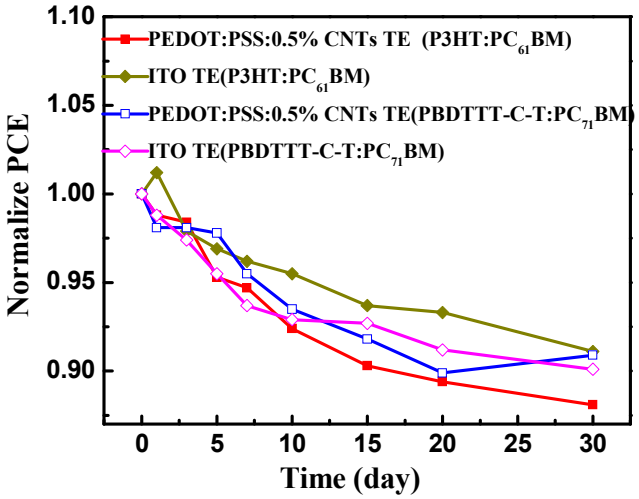

Figure S8. The normalized efficiency decay of P3HT:$PC_{61}BM$ and PBDTTT-C-T:$PC_{71}BM$ PSCs base on ITO and PEDOT:PSS:0.5%CNTs films as cathode at ambient atmosphere.

Table S4. Electrical and optical properties of the roll-to-roll printed PEDOT:PSS:CNTs electrode on PET substrate.

Ink	Web speed (m min^{-1})	Roll speed (m min^{-1})	Average Sheet resistance[a] (Ω sq^{-1})	Average Sheet resistance[b] (Ω sq^{-1})	Best Sheet resistance[b] (Ω sq^{-1})	Thickness (nm)[c]
PEDOT:PSS PH1000	0.20	0.16	112±42	98±18	80	45±10
	0.20	0.18	147±33	136±18	108	65±10
	0.20	0.20	178±24	95±14	81	110±10
	0.20	0.22	143±12	69±9	60	160±10
	0.30	0.24	85±22	81±16	65	40±7
	0.30	0.27	125±37	85±25	60	60±10
	0.30	0.30	170±10	122±10	112	100±10
	0.30	0.33	147±11	55±6	49	160±10
PEDOT:PSS PH1000:0.5 %CNTs	0.30	0.09	225±6	244±4	240	20±5
	0.30	0.18	136±4	135±5	130	30±7
	0.30	0.24	111±5	84±6	78	40±10
	0.30	0.30	100±5	44±5	39	100±10
	0.30	0.33	63±13	19±2	17	160±10
	0.30	0.36	64±5	27±2	25	170±10
Commercial ITO/PET				35±5	30	

[a]before annealing treatment; [b]after 130^{o}C annealing treatment; the figures of the average sheet resistance base on at least six point. [c] the Sheet resistance was tested only by a four point probe setup. [c]the thickness of R2R-prepared PEDOT:PSS/CNT composite layers were measured by surface profilometer (AMBIOS TECHNOLOGY ltd. XP-2).

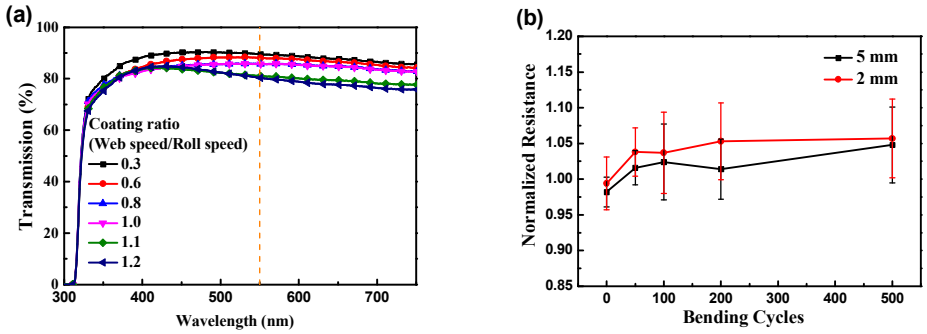

Figure S9. (a) The transmittance spectra of PEDOT:PSS:CNTs films via roll-to-roll process in the visible range, (b) Normalized resistance of printed lines over 500 bending cycles at a radius of curvature of 2 mm and 5 mm respectively.

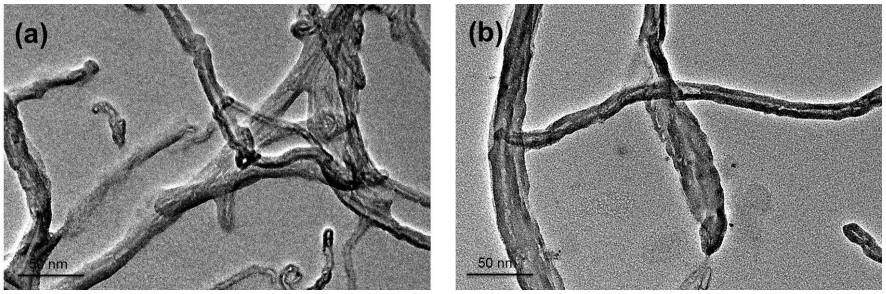

Figure S10. Transmission Electron Microscope (TEM) image of (a) pristine CNTs and (b) acidification CNTs.

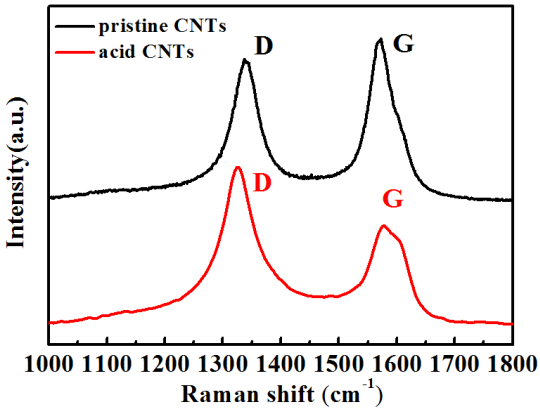

Figure S11. Raman spectra of pristine CNTs and acid CNTs. Raman spectroscopy was performed using an InVia Raman Microscope system (Renishaw, Inc.), with an Ar+ ion laser operating at 613 nm and 1.2 mW