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A Low-temperature carbon electrode with benign perovskite compatibility and high flexibility in Carbon based perovskite solar cells

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Experimental Section

1.Materials

All the chemicals were used directly without further purification. Titanium dioxide (TiO_2, NR-30) was purchased from The Great Solar Cell. Lead iodide (PbI_2, 99%); Lead bromide ($PbBr_2$, 99.999%); N, N-dimethyl formamide (DMF, 99.7%); dimethyl sulfoxide (DMSO, 99.7%); chlorobenzene (CB, 99%); titanium (IV) isopropoxide (TTIP, 99%); CsI (99.9%); glacial acetic acid (HAc) and α-terpineol (Terp) (mixture of isomers, anhyrous) were purchased from Aldrich. PEN substrates were purchased from YOUXUAN TECH. Tin(IV) oxide (SnO_2, 15% in H_2O colloidal dispersion) was purchased from Alfa Aesar. Formamidine iodide (FAI, 99.5%) and Methylammonium bromide (MABr, 99%) Methylammonium iodide (MAI, 99%) were purchased from Materwin of Shanghai. Dyesol fluorine-doped tin oxide conducting glass (FTO, Pilkington, thickness 2.2 mm, sheet resistance 15 $\Omega\ \square^{-1}$) was used as substrates for the solar cell. M125 PEDOT: PSS HTL Solar 3 was purchased from Ossila.

2.Preparation of Carbon electrodes

The carbon pastes were prepared as reported before. 4.5 g graphite and 1.5 g carbon black were uniformly dispersed in 10.0 g terpineol via ball milling for 2 h. Then, 1.83 ml TTIP and 0.2 ml HAC were added into the mixture by ball milling for another 10 h to gain homogenized carbon paste. The carbon electrodes were deposited using screen-printing method. The neatly arranged holes are scattered on a certain number of mesh screens, and then the devices are neatly attached to the back of the screen plate. Carbon paste is applied to the front of the screen plate and is brushed with proper force, the device is then removed quickly and is annealed at 70 ℃ for 1 h.

3.Preparation of HTM-free C-based Perovskite Solar Cells

The FTO conducting glass was etched with a laser to form desired electrode patterns before being ultrasonically cleaned with detergent solution, deionized water and ethanol for 15 minutes, respectively. Then, the clean FTO conducting glass was treated with ultraviolet ozone for 20 minutes with that a compact TiO_2 layer was deposited on

the substrate by a spray pyrolysis deposition method at 450 ℃ with a 2-propanol solution containing diisopropoxytitanium bis (acetylacetonate). Then, the annealed glass was treated with ultraviolet ozone for 20 minutes straight after a mesoporous TiO_2 layer (diluted in the terpineol with the ratio of 1:6) was screen printed on the substrate and was sintered at 500 ℃ for 40 minutes. After cooling down to room temperature, the glass was cut into 20 pieces with 2 mm long and 2.5 mm wide and after was treated with ultraviolet ozone for 20 minutes. The perovskite precursor solution was prepared by dissolving PbI_2, FAI, $PbBr_2$, MABr and CsI in mixed solvents with the ratio of DMF and DMSO is 4:1. And the $Cs_{0.05}(FA_{0.83}MA_{0.17})_{0.95}Pb(I_{0.83}Br_{0.17})_3$ was deposited on the TiO_2 as previously reported.[1] At last, the carbon layer was screen printed on the perovskite and annealed at 70 ℃ for 1 h.

4.Preparation of Adding PEDOT: PSS C-based Perovskite Solar Cells

Filtered PEDOT: PSS solution of toluene dispersion through 0.45 μm PTFE (hydrophobic) filter). The compact TiO_2 layer, mesoporous TiO_2 layer and perovskite layer were deposited on FTO glass as above. Then, higher speeds dynamic spin coating of PEDOT: PSS solution was deposited on the perovskite layer by spin-coating at 3000 rpm for >35 s to make the films dry in air. Once the spin coating has finished, placed the samples on the hotplate at 100 ℃ for 30 minutes to fully dry. Finally, the carbon layer was screen printed on the PEDOT: PSS and was annealed at 70 ℃ for 1 h.

5.Preparation of Flexible Perovskite Solar Cells

Filtered Tin (IV) oxide (SnO_2, 15% in H_2O colloidal dispersion) through 0.45 μm PTFE (hydrophobic) filter). The ITO/PEN substrate was ultrasonically cleaned with deionized water and ethanol for 15 minutes, respectively. Then, the substrate was treated with ultraviolet ozone for 20 minutes. Immediately, the SnO_2 (Diluted with the proportion of 1:5 in H_2O colloidal dispersion) was deposited on the PEN substrate at 3000 rpm for 30 s and then annealed at 100 ℃ for 30 minutes. After cooling down to room temperature, the SnO_2 substrate was treated with ultraviolet ozone for 20 minutes and then was transformed into the glove box quickly. The perovskite was deposited

on the SnO_2 as reported before. Then, the PEDOT: PSS layer was deposited by spin-coating at 3000 rpm for >35 s and placed the samples on the hotplate at 100 ℃ for 30 minutes to fully dry. Finally, the carbon layer was screen printed on the PEDOT: PSS and annealed at 70 ℃ for 1 h.

6.Characterizations

Sheet resistance of the carbon film was measured with a Signatone Lucaslabs 4-point resistivity probe fitted with a soft tip and small spring constant to prevent excessive damage to the film (SP4-40045TBY). The measurement was taken on three spots separated by around 1 cm and distributed across 1 x 1 cm^2 substrate. Photocurrent-density voltage (J-V) curves were characterized with a Keithley 2400 source meter and a Newport solar simulator (model 91192). The power of the simulated light was calibrated to 100mw cm^{-2} using a Newport Oriel PV reference cell (model 91150 V). The active area S3 of the device is about 0.8 cm^2 and a black mask with a circular aperture (0.102 cm^2) was applied for J-V measurements, smaller than the active area of the square solar cell (0.8 cm^2), was applied on top of the cell and the scan rate was 250 mV s^{-1}. The scanning electron microscopy (SEM) was performed with a field emission SEM (FEI Nova Nano SEM 450). Time-resolved photoluminescence (TRPL) decay transients were measured at 760 nm using excitation with a 478 nm light pulse from the HORIBA Scientific DeltaProfluorimeter. The incident photon conversion efficiency (IPCE) was measured using a 150 W xenon lamp (Oriel) fitted with a monochromator (Cornerstone 74004) as a monochromatic light source.

Supporting tables

Table S1 The time-resolved photoluminescence lifetime results of perovskite film and perovskite film after dealing with component solvents

	τ1/s	τ2/s	A1/%	A2/%	Lifetime/ns
before-1	8.60×10^{-9}	3.49×10^{-7}	0.63	99.37	346.80
before-2	8.50×10^{-9}	3.36×10^{-7}	0.65	99.35	333.81
before-3	7.16×10^{-9}	2.54×10^{-7}	0.89	99.11	251.74
1min-1	7.08×10^{-9}	2.92×10^{-7}	0.69	99.31	289.98
1min-2	7.00×10^{-9}	2.87×10^{-7}	0.70	99.30	285.00
1min-3	6.90×10^{-9}	2.78×10^{-7}	0.73	99.27	275.97
1min-4	6.91×10^{-9}	2.65×10^{-7}	0.80	99.20	262.88
2mins-1	7.23×10^{-9}	2.53×10^{-7}	0.91	99.09	250.70
2mins-2	7.61×10^{-9}	2.50×10^{-7}	0.99	99.01	247.53
2mins-3	6.87×10^{-9}	2.75×10^{-7}	0.75	99.25	272.94
2mins-4	7.05×10^{-9}	2.89×10^{-7}	0.70	99.30	286.98
5mins-1	6.89×10^{-9}	2.78×10^{-7}	0.74	99.26	275.94
5mins-2	6.90×10^{-9}	2.67×10^{-7}	0.78	99.22	264.92
5mins-3	6.99×10^{-9}	2.59×10^{-7}	0.84	99.16	256.82
5mins-4	7.73×10^{-9}	2.50×10^{-7}	1.93	98.99	247.48

Table S2 The one of photovoltaic properties of hole-conductor-free perovskite solar cells based on low temperature carbon electrodes

	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)	Hysteresis index
Reverse	900	19.93	0.65	11.74	0.248
Forward	860	19.46	0.53	8.88	

Table S3 The one of photovoltaic properties of perovskite solar cells with adding a PEDOT: PSS layer based on low temperature carbon electrodes

	V_{OC} (mV)	J_{SC} (mA cm^{-2})	FF	η (%)	Hysteresis index
Reverse	920	21.37	0.72	14.26	0.069
Forward	890	21.26	0.69	13.01	

Table S4 The time-resolved photoluminescence lifetime results of perovskite (pvk) film, perovskite/C, perovskite/PEDOT: PSS and perovskite/PEDOT: PSS/C

	τ1/s	**τ2/s**	**A1/%**	**A2/%**	**Lifetime/ns**
pvk-1	8.60×10^{-9}	3.49×10^{-7}	0.63	99.37	346.80
pvk-2	8.50×10^{-9}	3.36×10^{-7}	0.65	99.35	333.81
pvk-3	7.16×10^{-9}	2.54×10^{-7}	0.89	99.11	251.74
pvk-C-1	4.34×10^{-9}	9.02×10^{-8}	6.90	93.10	83.89
pvk-C-2	4.40×10^{-9}	9.10×10^{-8}	6.93	93.70	85.26
pvk-C-3	4.42×10^{-9}	9.12×10^{-8}	6.95	93.05	84.86
pvk-PEDOT: PSS-1	3.63×10^{-9}	3.40×10^{-8}	30.20	69.98	23.79
pvk-PEDOT: PSS-2	3.61×10^{-9}	3.38×10^{-8}	29.89	70.11	26.06
pvk-PEDOT: PSS-3	3.38×10^{-9}	3.23×10^{-8}	28.73	71.27	23.02
pvk-PEDOT: PSS-C-1	3.38×10^{-9}	2.26×10^{-8}	32.46	65.74	14.86
pvk-PEDOT: PSS-C-2	3.61×10^{-9}	2.39×10^{-8}	34.31	65.69	15.77
pvk-PEDOT: PSS-C-3	3.65×10^{-9}	2.40×10^{-8}	34.57	65.43	15.60

Table S5 The sheet resistance of the low temperature carbon film before and after 100 bends

	Initial ($\Omega\ \square^{-1}$)				after 100 bends ($\Omega\ \square^{-1}$)			
Sample	1	2	3	4	1	2	3	4
Point A	16.8	10.2	26.5	11	17.1	10.6	26.5	11.6
Point B	18.2	12	18.4	9.8	18.3	11.7	18.4	10.5
Point C	16.5	13	18.9	11.8	16.7	13.2	18.9	11.4
Average	17.2	11.7	21.3	10.9	17.4	11.8	21.3	11.2
Stdev	0.7	1.2	3.7	0.8	0.7	1.1	3.7	0.5

Supporting figures

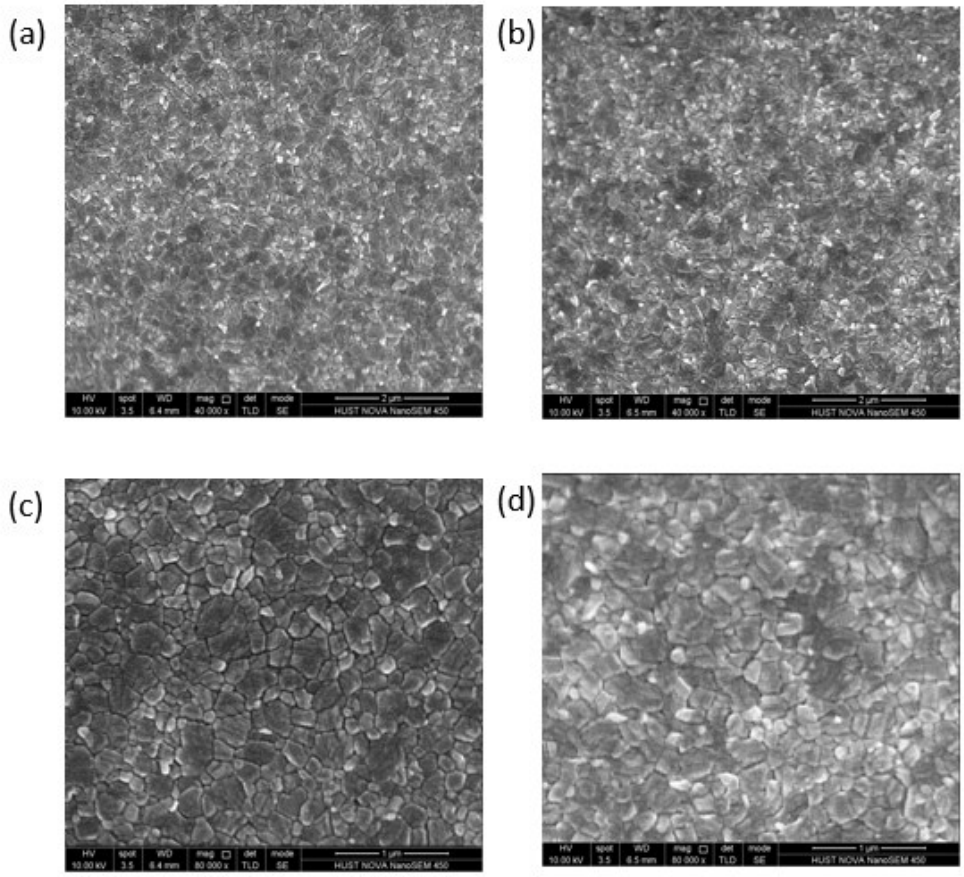

Fig. S1 (a-d) The surface SEM image of the perovskite film before and after treatment with component solvents.

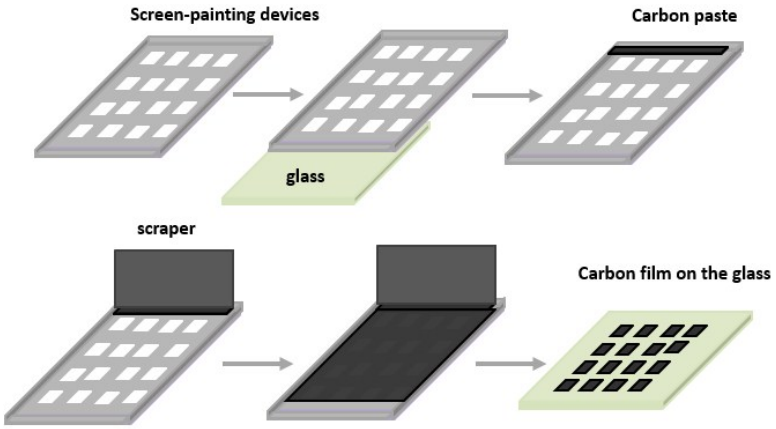

Fig. S2 The manufacturing process of screen-painting carbon.

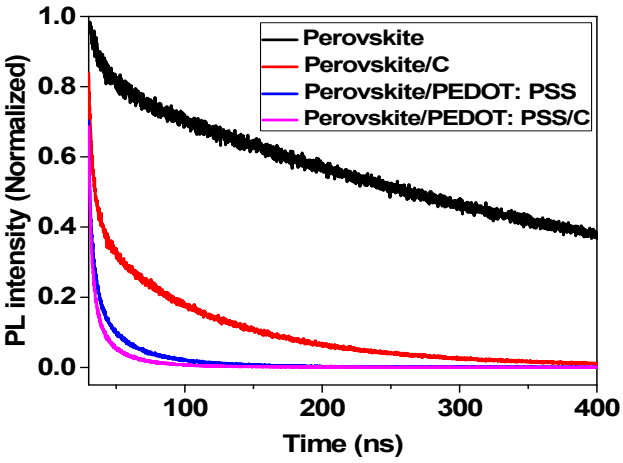

Fig. S3 The TRPL decays of perovskite film, perovskite/C, perovskite/PEDOT: PSS, and perovskite/PEDOT: PSS/C.

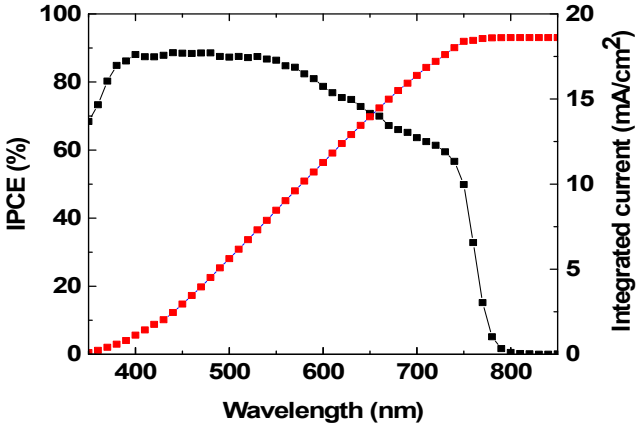

Fig. S4 The IPCE and integrated current density of the typical solar cell device.

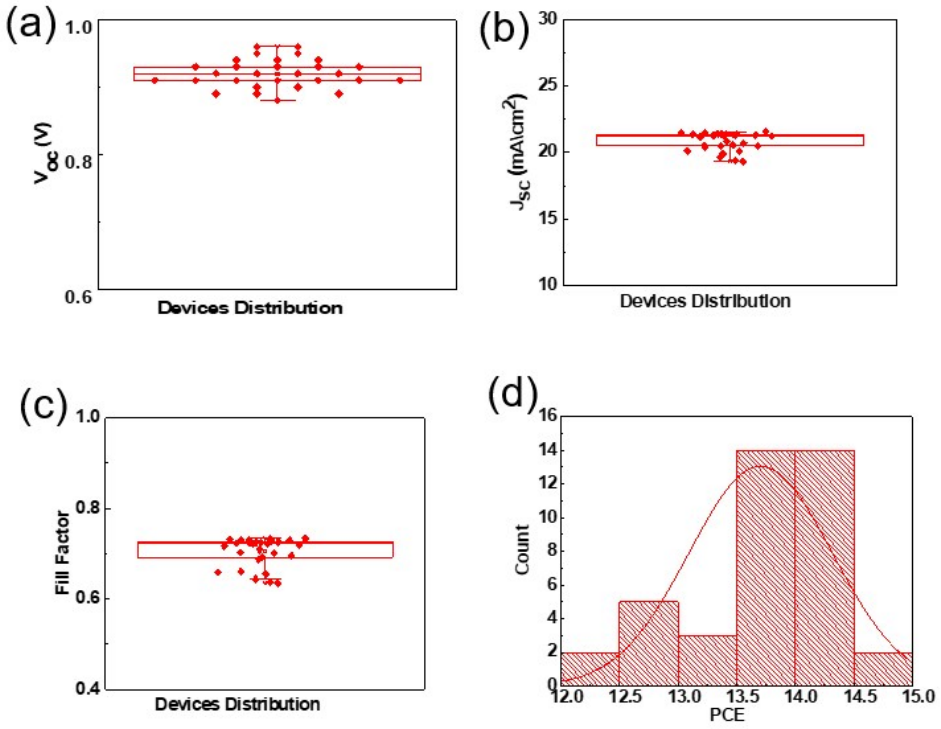

Fig. S5 The box diagram of V_{OC} (a), J_{SC} (b), FF (c) about the parameters of battery performance, (d) the histogram bar graph and normal distribution of PCE about 40 pieces of perovskite solar cells.

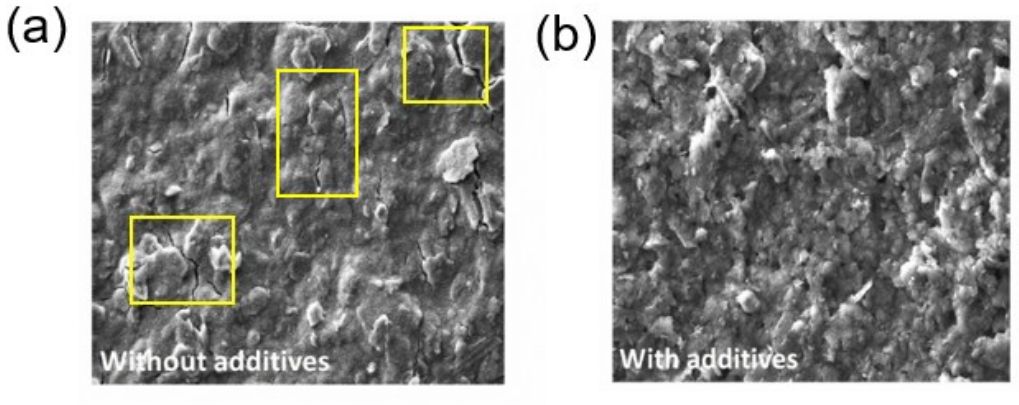

Fig. S6 The surface SEM characterization of low temperature carbon film without the treatment (a) and with the treatment of mixed functional additives (b).

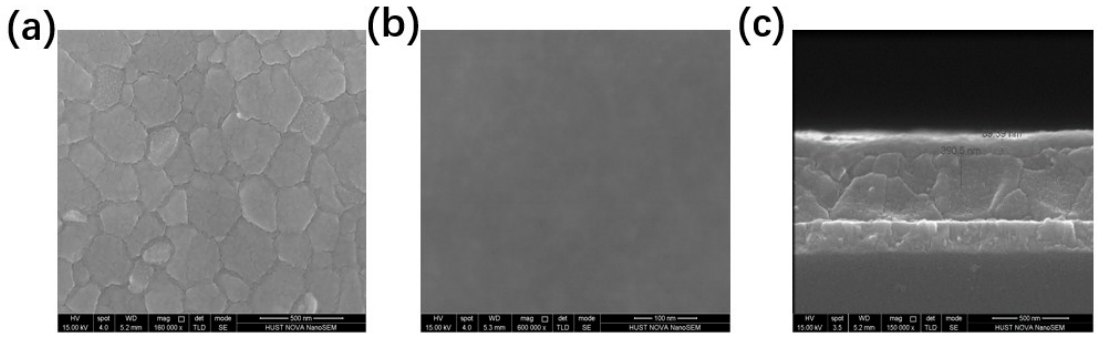

Fig. S7 (a) The surface SEM characterization of perovskite. (b)The surface SEM characterization of PEDOT: PSS. (c) The cross section SEM image of the ITO/perovskite/PEDOT: PSS on glass.

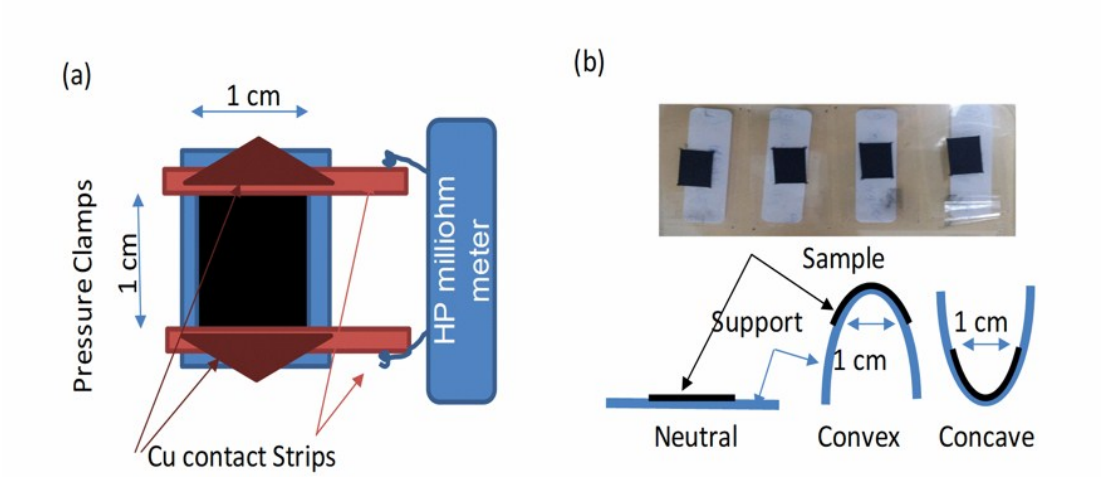

Fig. S8 The schematic diagram of equipment for testing mechanical strength (flexibility) of low temperature carbon paste film. (b) the preparation of the sample and the diagram of bending state and bending angle.[2]

References

1. M. Saliba, T. Matsui, J.-Y. Seo, K. Domanski, J.-P. Correa-Baena, M. K. Nazeeruddin, S. M. Zakeeruddin, W. Tress, A. Abate and A. Hagfeldt, *Energy Environ. Sci.*, 2016, **9**, 1989-1997.
2. P. Jiang, T. W. Jones, N. W. Duffy, K. F. Anderson, R. Bennett, M. Grigore, P. Marvig, Y. Xiong, T. Liu and Y. Sheng, *Carbon*, 2018, **129**, 830-836.