

## Electronic Supplementary Information

# Fluorine Plasma Treatment on Carbon-based Perovskite Solar Cells for Rapid Moisture Protection Layer Formation and Performance Enhancement

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## Experimental details

**Materials:** If not otherwise noted, all chemical reagents and solvents were purchased from Sigma Aldrich and used without further purification. Fluorine doped tin oxide (FTO,  $7 \Omega \text{ sq}^{-1}$ ) coated glass was purchased from Wooyang GMS.  $\text{TiO}_2$  paste (30 NR-D), Methylammonium bromide (MABr,  $\text{CH}_3\text{NH}_3\text{Br}$ ), and Formamidinium iodide (FAI,  $\text{CH}(\text{NH}_2)_2\text{I}$ ) were purchased from GreatCell Solar. Carbon black (Super-P conductive) and Lead iodide ( $\text{PbI}_2$ , 99.9985 %) were purchased from Alfa Aesar. Carbon paste (FTU-16,  $\leq 20 \Omega \text{ sq}^{-1}$ ) was purchased from Asahi Chemical Research Laboratory.

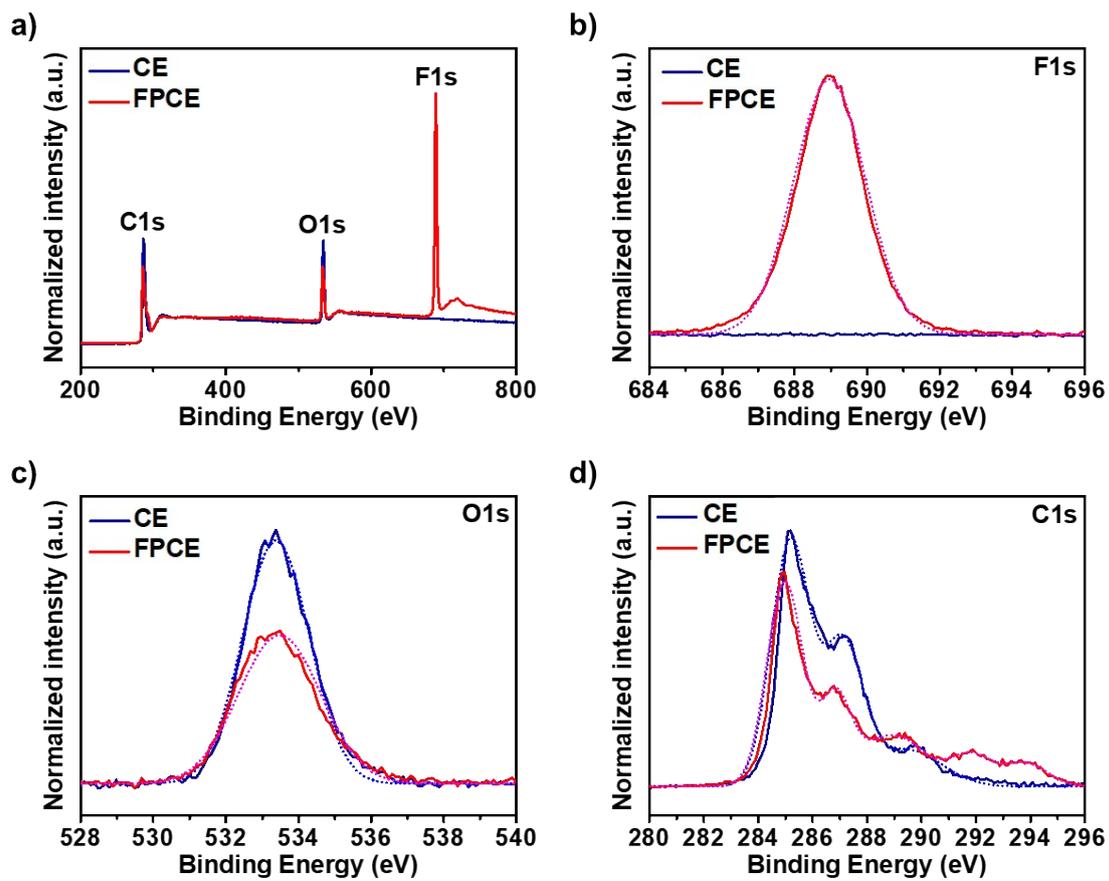
**Device Fabrication:** FTO glass substrates were etched with 2.0 M aqueous HCl and Zn powder to form the patterned electrode. The patterned FTO substrates were ultrasonically cleaned in deionized water, acetone and isopropyl alcohol for 60 min, sequentially. To deposit a compact  $\text{TiO}_2$  layer (c- $\text{TiO}_2$  layer) for a hole-blocking, a solution of titanium (IV) isopropoxide (1 ml) in 15 ml mixed solution of Ethanol:HCl (4:1 at a volumetric ratio) was spin coated onto the substrate at 3000 rpm for 30 s and preheated at 120 °C for 10 min in ambient air. The preheated substrate was sintered at 500 °C for 60 min in a muffle furnace and then cooled at room temperature. A solution of  $\text{TiO}_2$  paste, which was diluted in ethanol (1:3.5 at molar ratio) to form a mesoporous  $\text{TiO}_2$  layer (meso- $\text{TiO}_2$ ), was spin coated on the c- $\text{TiO}_2$  layer at 3000 rpm for 30s. The substrate was annealed at 150 °C for 10 min and then sintered at 500 °C for 60 min. To prepare Li-doped  $\text{TiO}_2$ , lithium bistrifluoro-methanesulfonimide solution (Li-TFSI, 15 mg/ml in acetonitrile) was treated on the meso- $\text{TiO}_2$  layer by spin coating at 3000 rpm for 30 s. The treated substrate was preheated at 150 °C for 10 min, followed by sintering process at 500 °C for 30 min. The mixed perovskite ( $\text{Cs}_{0.05}\text{MA}_{0.16}\text{FA}_{0.79}\text{Pb}(\text{I}_{0.84}\text{Br}_{0.16})_3$ ) precursor solution was prepared by mixing the  $\text{PbI}_2$  (1.1 M),  $\text{PbBr}_2$  (0.2 M), FAI (1 M), MABr (0.2 M), and CsI (0.06 M) in a mixed solvent of DMF:DMSO (4:1 at a volumetric ratio). The mixed

solution was stirred at 60 °C for 2 h and filtered with 0.45 µm PTFE syringe filter before spin coating. The prepared perovskite precursor solution spread onto the substrate and spin coated by two steps process at 1000 and 4000 rpm for 10 and 23 s, respectively. After entering the second step, 180 µl of chlorobenzene was poured onto the substrate 10 seconds before the end of the process. After the entire spin coating process is completed, the substrate is placed on a 100 °C hot plate and annealed for 30 minutes to crystallize the perovskite layer. To form the carbon electrode, a carbon paste mixed with carbon black (2 wt %) was screen printed on the perovskite layer, and the printed carbon paste was dried at 80 °C for 10 minutes. This carbon printing process was repeated three times successively. To introduce fluorine atoms into the carbon electrode, a fluorine vacuum plasma treatment was performed on the substrate on which the carbon electrode was printed. In the plasma system (Korea vacuum Co.), which was used in experiments, an ICP (inductively coupled plasma) source was formed with RF power in a vacuum vessel. The fluorine source, C<sub>4</sub>F<sub>8</sub> gas, was flowed at a rate of 5 sccm under 25 Pa and treated with 100 W power for 20 minutes. The fluorine source injection conditions were optimized based on previous reports.<sup>s1</sup> With the exception of the plasma treatment, all manufacturing processes were carried out under controlled atmospheric conditions with a relative humidity of 25 °C and 30%.

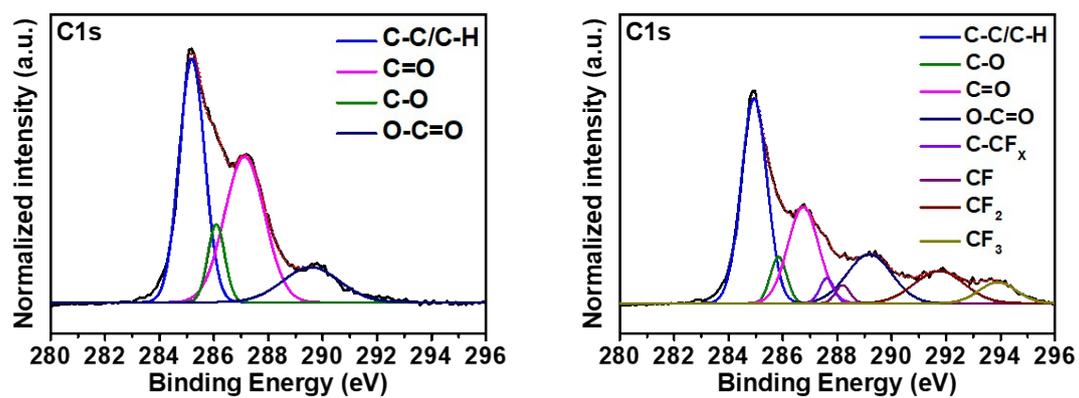
**Characterization:** The SEM-EPMA elemental mapping image and cross-sectional image were measured by JXA-8530F (JEOL) which is installed at the National Center for Inter-university Research Facilities (NCIRF) at Seoul National University. The XPS spectra of the carbon electrode were characterized by AXIS-Hsi (SHIMAZU-Kratos) and the FT-IR spectra of the carbon electrode were measured by Spotlight 200i (Perkinelmer) which are installed at the chemical and biological engineering research facilities (CBERF) at Seoul National University. The Raman spectra were measured by DXR2xi, which is installed at the National

Center for Inter-university Research Facilities (NCIRF) at Seoul National University. The UPS measurements were obtained by PHI 5000 Versa Probe, which is installed at the KIST Advanced Analysis Center at Korea Institute of Science and Technology. Time-resolved photoluminescence spectra were characterized under exposure to 520 nm pulse laser (PicoQuant). The photovoltaic properties of the PSCs were measured using  $I$ - $V$  tracer (MP-160) under standard AM 1.5 G (100 mW cm<sup>-2</sup>) illumination from a xenon lamp (500 W), calibrated with a KG 5-filtered Si reference cell (K 801; McScience Inc). The IPCE spectra were measured using K3100 Solar Cell IPCE System (McScience) without bias light. Open-circuit voltage ( $V_{OC}$ ) at the light condition, and electrochemical impedance spectra (EIS) of the PSCs were characterized by the Zive Lab equipment (WonATech). The measured EIS spectrum was fitted to equivalent electrical circuits using the Z-view analyst software (ZMAN). The apparent contact angles of deionized water on the untreated and fluorine plasma treated carbon electrode surfaces were measured by SmartDrop (FEMTOFAB Co., Korea). The perovskite surface change of the active layer after immersion in water was observed using an optical microscope (Lv100 microscope; Nikon).

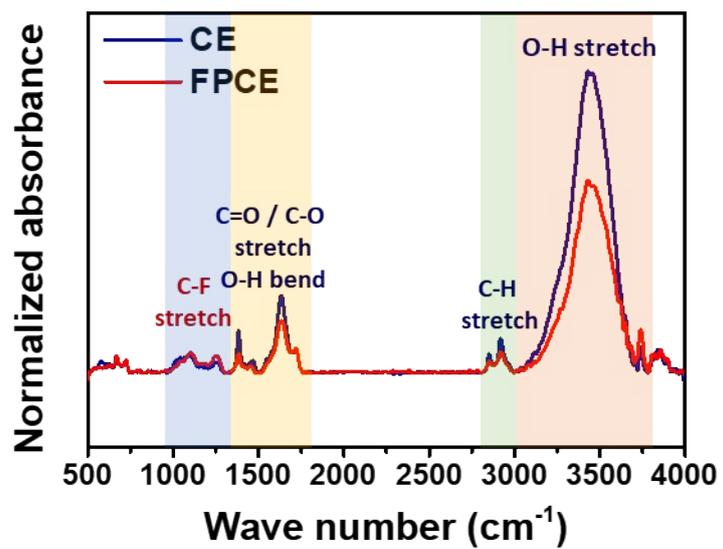
S1. C. Lee, Y.-J. Han, Y. D. Seo, K. Nakabayashi, J. Miyawaki, R. Santamaría, R. Menéndez, S.-H. Yoon and J. Jang, *Carbon*, 2016, **103**, 28-35.



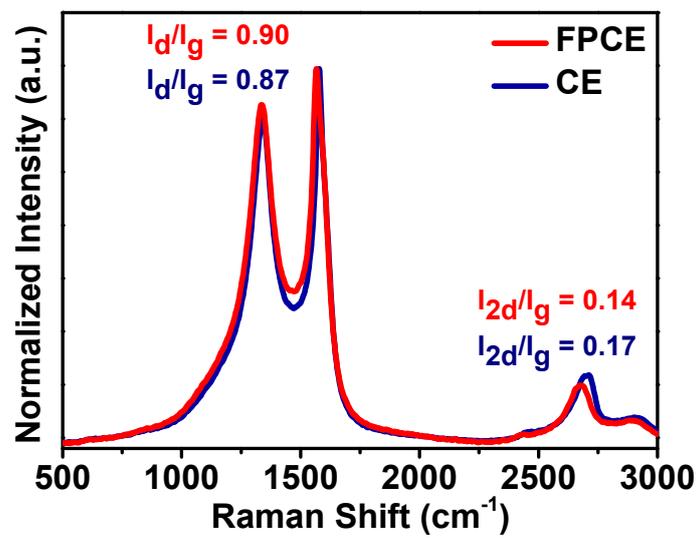
**Fig. S1** XPS spectra of CE and FPCE. a) XPS Survey spectra, b) – d) F1s, O1s, and C1s XPS spectra, respectively.



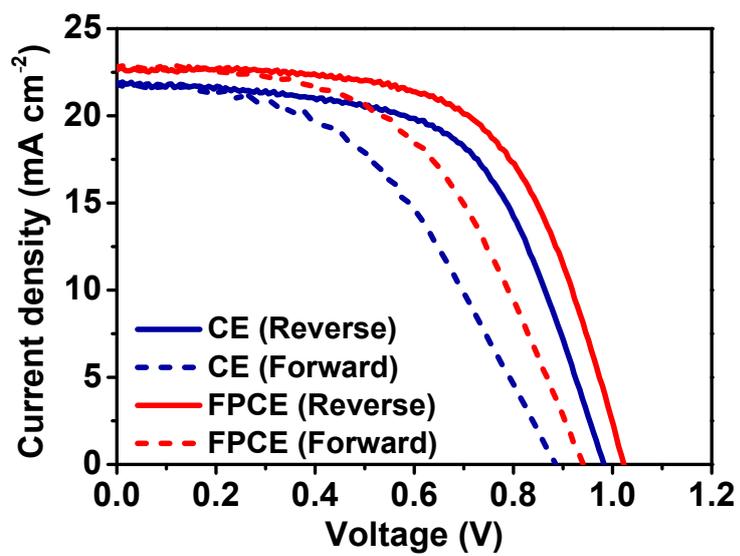
**Fig. S2** XPS spectra showing deconvolution curves of C1s without F plasma treatment (left) and with F plasma treatment (right), respectively.



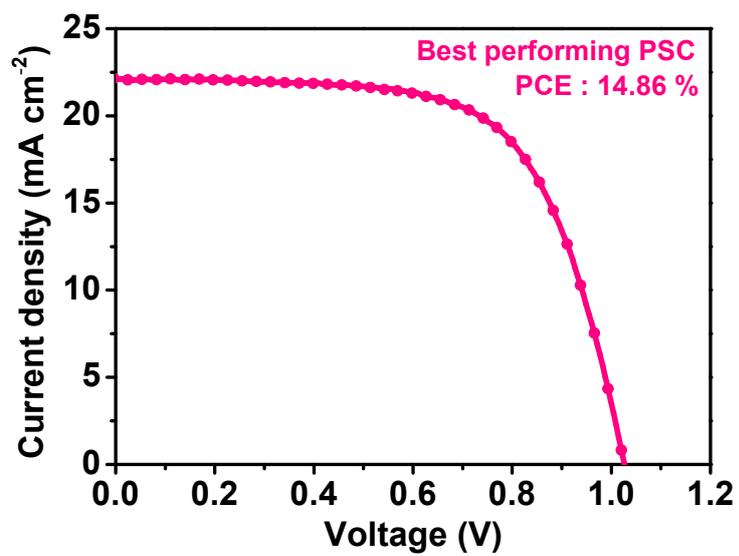
**Fig. S3** FT-IR spectra of CE and FPCE.



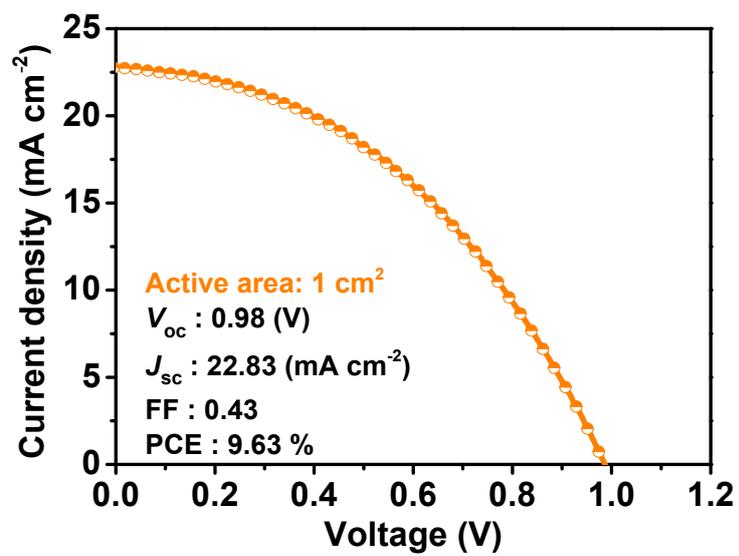
**Fig. S4** Raman spectra and calculated intensity ratio of CE and FPCE.



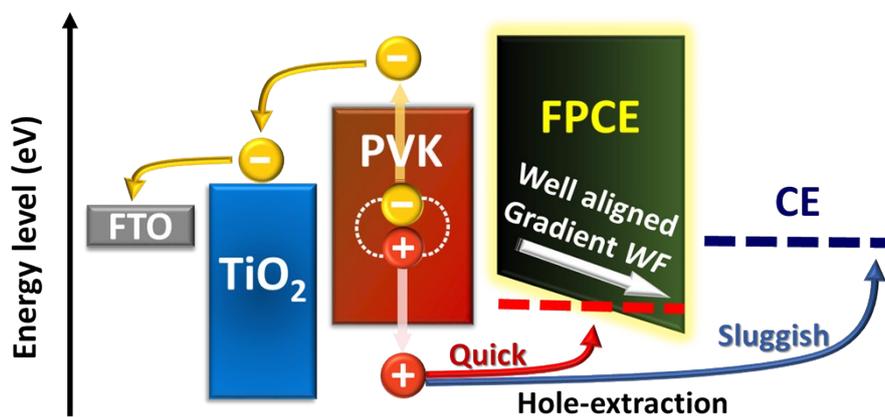
**Fig. S5** Current density–voltage ( $J$ – $V$ ) characteristics of carbon-based PSCs w/o and with F plasma treatment as a function of scan direction.



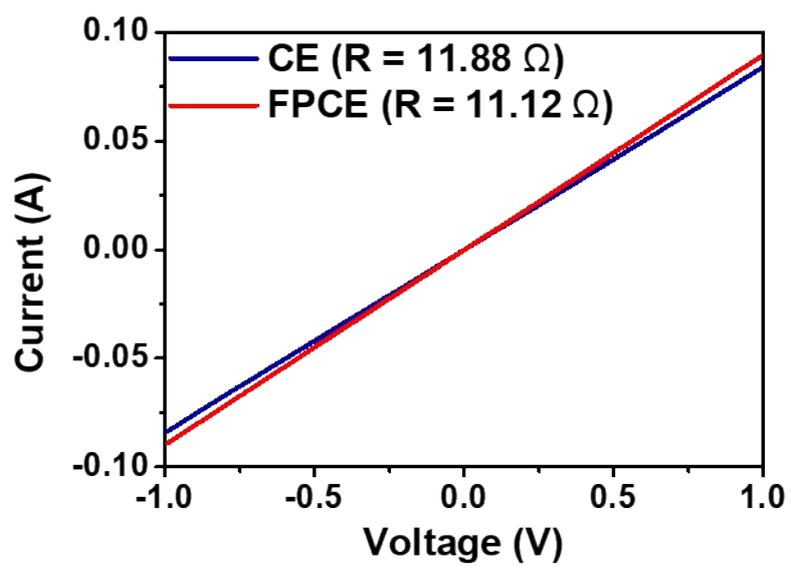
**Fig. S6**  $J$ - $V$  characteristics of the best-performing device (active layer size: 0.132 cm<sup>2</sup>).



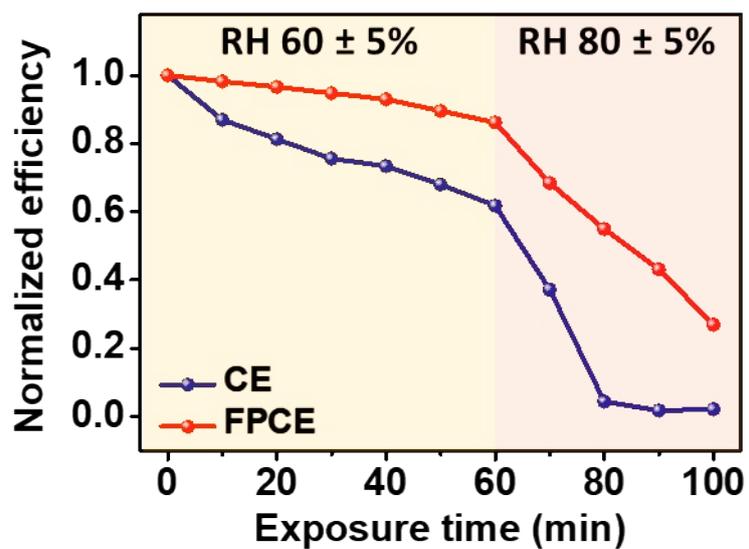
**Fig. S7**  $J$ - $V$  characteristics of the device with an active area of 1 cm<sup>2</sup>.



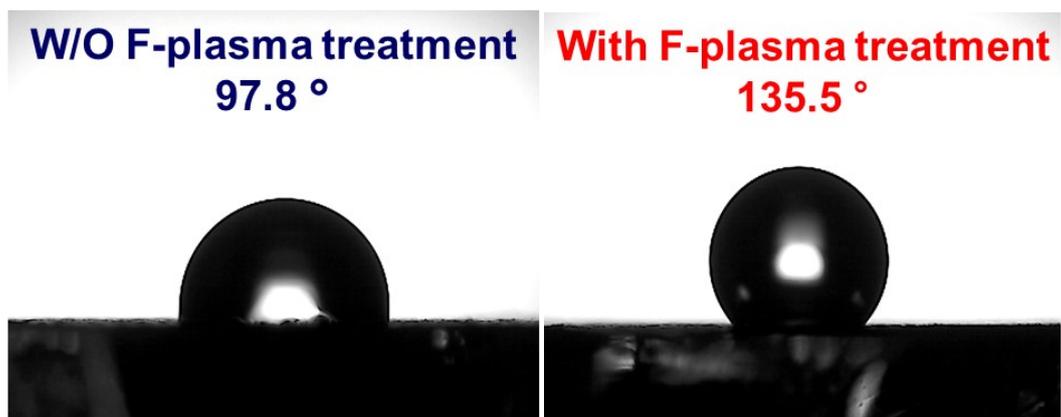
**Fig. S8** Energy band diagram of each component in the fabricated carbon-based perovskite solar cell (PSC) with or without F-plasma treatment, showing the separation and transport of photo-generated carriers.



**Fig. S9** *I-V* curves of the carbon electrode without and with F plasma treatment.



**Fig. S10** Stability test of the CE and FPCE devices under high humidity conditions (temperature: 25 °C; relative humidity: 60 and 80 ± 5 %)



**Fig. S11** Water contact angles w/o and with F plasma treatment on the carbon electrode.

**Table S1.** Elemental composition of the carbon electrode w/o and with F plasma treatment (CE and FPCE).

Sample	XPS (%)				
	C	O	F	F/C <sub>Ratio</sub>	O/C <sub>Ratio</sub>
CE	80.06	19.94	-	-	0.25
FPCE	57.97	11.07	30.96	0.53	0.19

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Sample	Assignment	Raman shift (cm <sup>-1</sup> )	FWHM
CE	D	1342.66	226.63
	G	1577.94	94.81
	2D	2701.27	122.77
FPCE	D	1334.95	235.08
	G	1566.36	98.62
	2D	2675.11	114.53

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**Table S2.** Raman spectra peak positions and intensity ratio.

**Table S3.** Photovoltaic parameters of carbon-based PSCs w/o and with F plasma treatment.

Device	Scan direction	$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)
CE	Forward	0.89	21.81	0.45	8.77
	Reverse	0.98	21.90	0.58	12.50
FPCE	Forward	0.94	22.78	0.50	10.81
	Reverse	1.02	22.66	0.60	13.97

**Table S4.** Photovoltaic parameters of best performing carbon-based PSCs with F plasma treatment.

Device		$V_{oc}$ (V)	$J_{sc}$ ( $\text{mA cm}^{-2}$ )	FF	PCE (%)
FPCE	Best	1.03	22.20	0.65	14.86
	Average	$1.02 \pm 9.79$	$21.38 \pm 0.50$	$0.65 \pm 0.015$	$14.07 \pm 0.33$

**Table S5.** Time-resolved photoluminescence (TRPL) decay parameters for the perovskite films w/o and with F plasma treatment on the carbon electrode. The curves were fitted with the bi-exponential decay equation.

Samples	$\tau_1$ (ns)	$\tau_2$ (ns)	${}^a)\tau_{\text{avg}}$ (ns)	A1	A2
Glass / TiO <sub>2</sub> / Perovskite / CE	3.98	78.32	77.62	0.11	0.56
Glass / TiO <sub>2</sub> / Perovskite / FPCE	3.97	37.34	34.51	0.43	0.49

$${}^a)\tau_{\text{avg}} = \frac{\sum_i A_i \tau_i^2}{\sum_i A_i \tau_i}$$

**Table S6.** Electrochemical impedance spectra (EIS) results of w/o and with F plasma treatment on the carbon-based PSC.

Device	$R_s$ ( $\Omega \text{ cm}^2$ )	$R_{ct}$ ( $\Omega \text{ cm}^2$ )
Untreated carbon-based PSC	20.46	97.45
F plasma-treated carbon- based PSC	17.46	86.27