Electronic Supplementary Material

Interface engineering of plasmonic induced Fe/N/C-F catalyst with enhanced oxygen catalysis performance for fuel cells application

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Experimental

Preparation of Fe/N/C-CNT catalyst.

Multi-walled carbon nanotubes (MWCNTs, purchased from Xianfeng Nano Co. Ltd. average diameter: 30-50 nm, length: 0.5-2 μm) were treated with nitric acid solution refluxed in an oil bath at 80 °C for 12 h, and washed with deionized water then dried at 80 °C for overnight under vacuum.

100 mg pretreated MWCNTs, and a certain amount of FePc was added into 75 ml of methanol solution and then ultrasonicated for two hours to obtain a uniformly dispersed suspension. 1700 mg of $Zn(NO_3)_2 \cdot 6H_2O$ was dissolved into the mixture and stirred at room temperature for two hours. After that, 75 mL methanol solution of 0.65 mol L^{-1} 2-methylimidazole was rapidly added to the above solution under stirring for 24 hours at room temperature. The precipitant was collected by washed with methanol and finally vacuum-dried, followed by an annealing process in a tube furnace at 900 ºC for one hour under nitrogen. After cooling to room temperature, the black power was pyrolyzed in an NH_3 atmosphere at 900 ºC for one hour, and the final product was labeled as Fe/N/C-CNT.

CF_4 plasma modification of Fe/N/C-CNT catalyst.

The plasma treatment was carried out in a plasma apparatus (MTI Co. Ltd.) at room temperature. The typical plasma irradiation process is as follows: the sample was placed on the sample stage, and the chamber was evacuated. A gas flow of carbon tetrafluoride (CF_4) was introduced into the chamber to reach 0.19 Torr for the plasma ignition. The applied frequency was 13.56 MHz with a radio frequency power of 60W, and the samples were treated for 60s. The resultant product was named Fe/N/C-CNT-F catalyst.

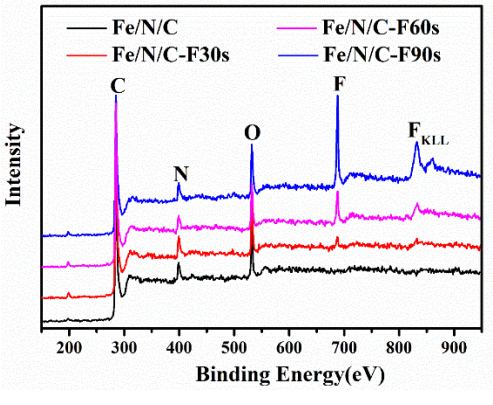

Figure S1 XPS spectra of the surface chemical composition of Fe/N/C and Fe/N/C-F catalysts.

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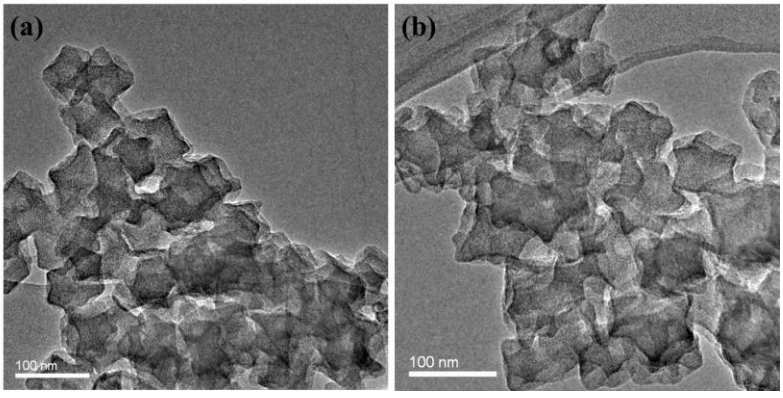

Figure S2 TEM images of (a) Fe/N/C and (b) Fe/N/C-F60s.

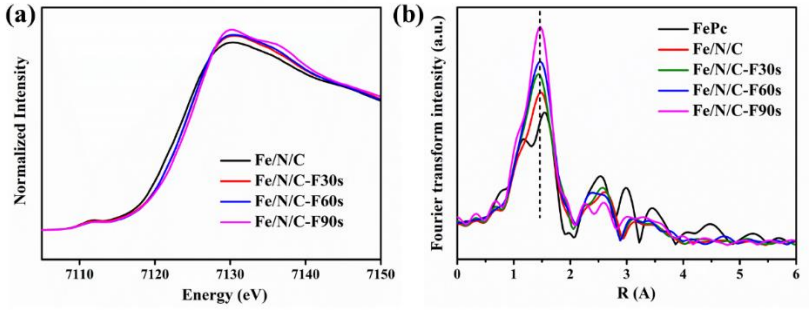

Figure S3 (a) Fe *K*-edge XANES and (b) Fourier transformed K_3-weighted EXAFS spectra of Fe/N/C and Fe/N/C-F catalysts.

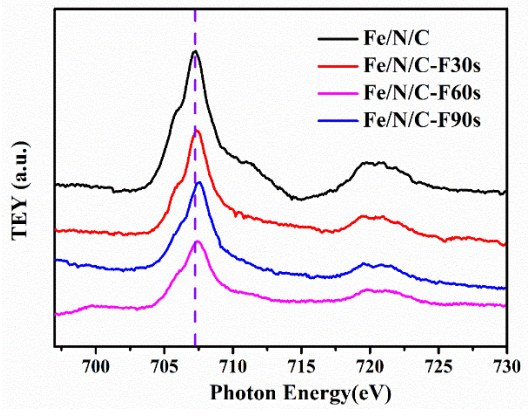

Figure S4 Fe *L*-edge XANES spectrum of Fe/N/C and Fe/N/C-F catalysts.

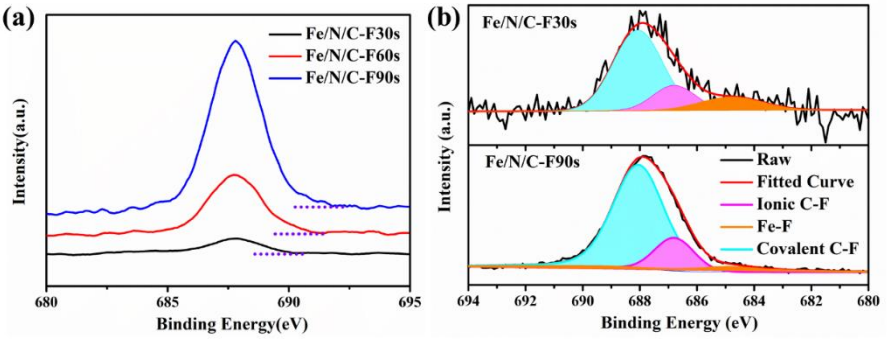

Figure S5 (a) XPS F 1s spectra of Fe/N/C-F catalysts. (b) XPS F 1s spectra of Fe/N/C-F30s and Fe/N/C-F90s.

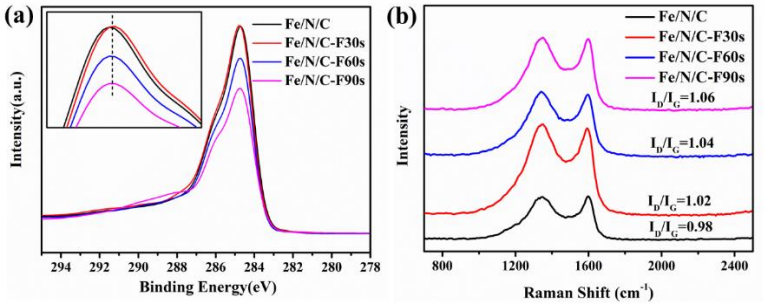

Figure S6 (a) XPS C 1s spectra of Fe/N/C and Fe/N/C-F catalysts. (b) Raman spectra of Fe/N/C and Fe/N/C-F catalysts.

Raman analysis was performed on each sample to understand the effect of CF_4 plasma treatment on the carbon structure of these catalysts. As shown in Figure S6b, the D bands at ~1340 cm^{-1} are associated with the disorder-induced carbon, and a G band approximately 1580 cm^{-1} corresponding to the sp^2 hybridized graphitic carbon. The ratio of intensity I_D/I_G increased from 0.98 to 1.06 with the increase of plasma time, indicating that the incorporation of fluorine atoms into the carbon structure of Fe/N/C induced the generation of structural defect sites by broad C−C bond polarization, thereby modifying the surface charge of the carbon structure.

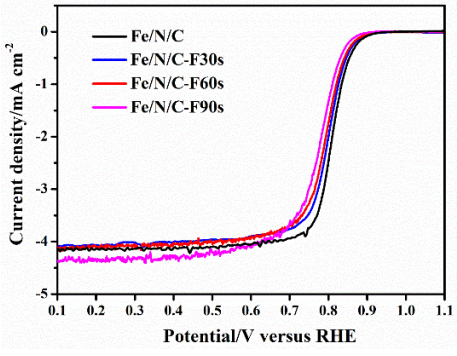

Figure S7 ORR polarization curves of Fe/N/C-F catalysts in O_2-saturated 0.5M H_2SO_4 at a scan rate of 5mV s^{-1}.

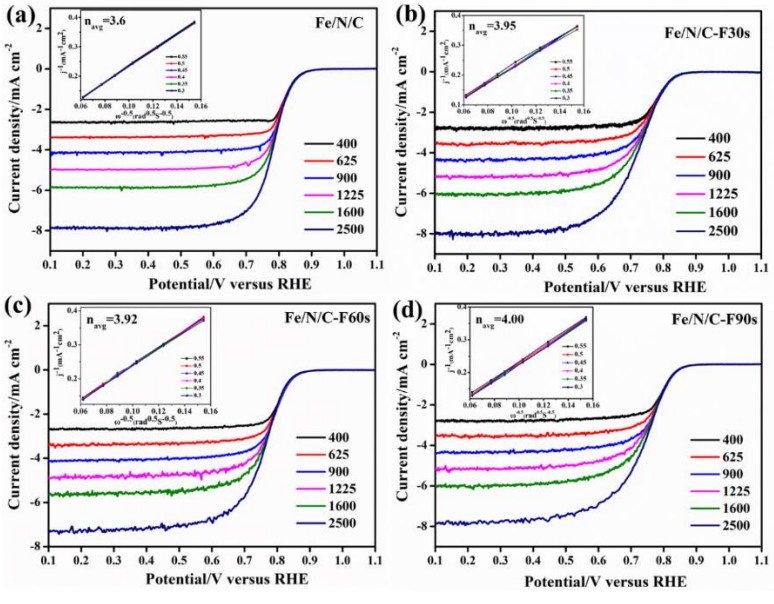

Figure S8 LSV curves at various rotation rates and the corresponding of K-L polts in O_2-saturated 0.5M H_2SO_4 for (a) Fe/N/C, (b) Fe/N/C-F30s, (c) Fe/N/C-F60s, (d) Fe/N/C-F90s.

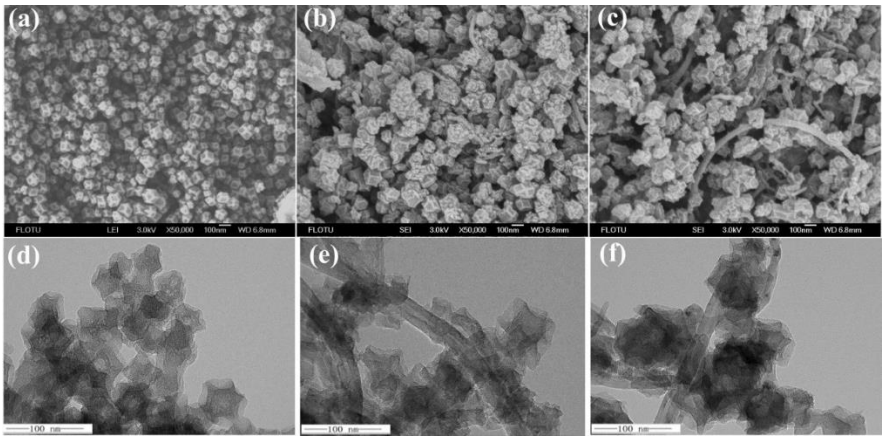

Figure S9 SEM images of (a) Fe/N/C, (b) Fe/N/C-CNT, (c) Fe/N/C-CNT-F. TEM images of (d) Fe/N/C, (e) Fe/N/C-CNT, (f) Fe/N/C-CNT-F.

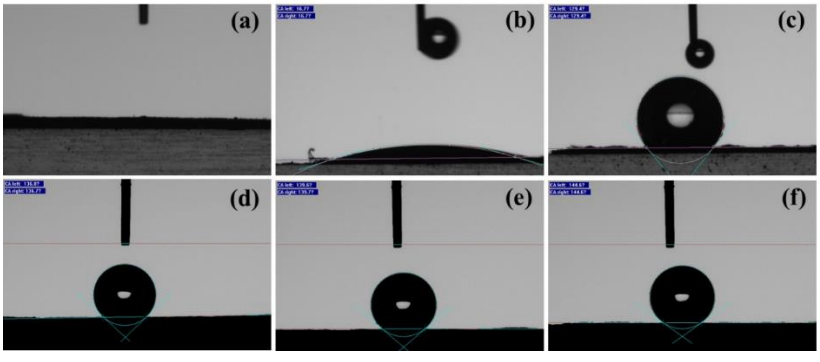

Figure S10 Contact angle of a water droplet on (a) Fe/N/C, (b) Fe/N/C-CNT, (c) Fe/N/C-CNT-F. Contact angle of a water droplet on (d) Fe/N/C, (e) Fe/N/C-CNT, (f) Fe/N/C-CNT-F cathode catalyst layer.

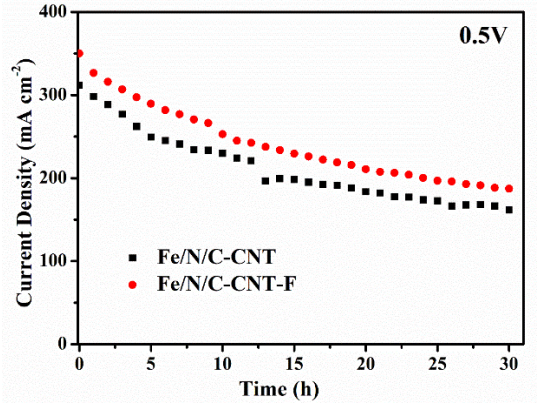

Figure S11 Accelerated stress tests at a constant voltage of 0.5 V in single H_2/O_2 PEMFCs with ambient pressure of H_2/O_2.

Table S1 XPS surface elemental analysis of the Fe/N/C and Fe/N/C-F.

	C	N	O	F	Fe
Fe/N/C	81.85	6.96	10.11	-	1.08
Fe/N/C-F30s	80.14	6.94	9.02	2.91	0.99
Fe/N/C-F60s	77.99	6.92	8.41	5.7	0.98
Fe/N/C-F90s	70.62	6.48	8.21	13.63	1.06

Table S2 Specific surface area, porosity properties, and electrical conductivity of the catalysts.

	Surface area ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Electrical conductivity ($S cm^{-1}$)
Fe/N/C	1242.6	1.29	0.026
Fe/N/C-F30s	1133.7	1.27	0.032
Fe/N/C-F60s	1137.7	1.21	0.037
Fe/N/C-F90s	1097.6	1.20	0.037
CNTs	-	-	0.293
Fe/N/C-CNT	638.9	0.97	0.231
Fe/N/C-CNT-F	543.1	0.96	0.247

Table S3 The change of |△G| in each elementary reaction step.

Elementary Reactions	|ΔG| (eV)					
	U=0V		U=0.66V		U=0.72V	
	$Fe-N_4$	$F-Fe-N_4$	$Fe-N_4$	$F-Fe-N_4$	$Fe-N_4$	$F-Fe-N_4$
$O_2(g)+H^++e^-+*\rightarrow OOH*$	0.66	0.94	0	0.28	0.06	0.22
$OOH*+H^++e^-\rightarrow O*+H_2O(l)$	2.49	1.69	1.83	1.03	1.77	0.97
$O*+H^++e^-\rightarrow OH*$	0.68	1.45	0.02	0.79	0.04	0.73
$OH*+H^++e^-\rightarrow H_2O(l)+*$	0.97	0.72	0.31	0.06	0.25	0

Table S4 Summary of the ORR activity parameters at an electrode rotation speed of 900 rpm in O_2-saturated 0.5M H_2SO_4 at a scan rate of 5 $mV s^{-1}$.

	Initial Potential (V vs RHE)	Half-Wave Potential (V vs RHE)
Fe/N/C	0.934	0.809
Fe/N/C-F30s	0.934	0.800
Fe/N/C-F60s	0.924	0.792
Fe/N/C-F90s	0.904	0.777
Pt/C	0.958	0.830

Table S5 Catalyst contact angle and catalyst layer contact angle of the samples.

	Catalyst contact angle of water droplet	Catalyst layer contact angle of water droplet
Fe/N/C	0	136±2.7
Fe/N/C-CNT	16±1.8	138±3.1
Fe/N/C-CNT-F	129±4.3	144±2.5