Electronic supplementary information:

Plasma-etched functionalized graphene as a metal-free electrocatalyst in solid acid fuel cells

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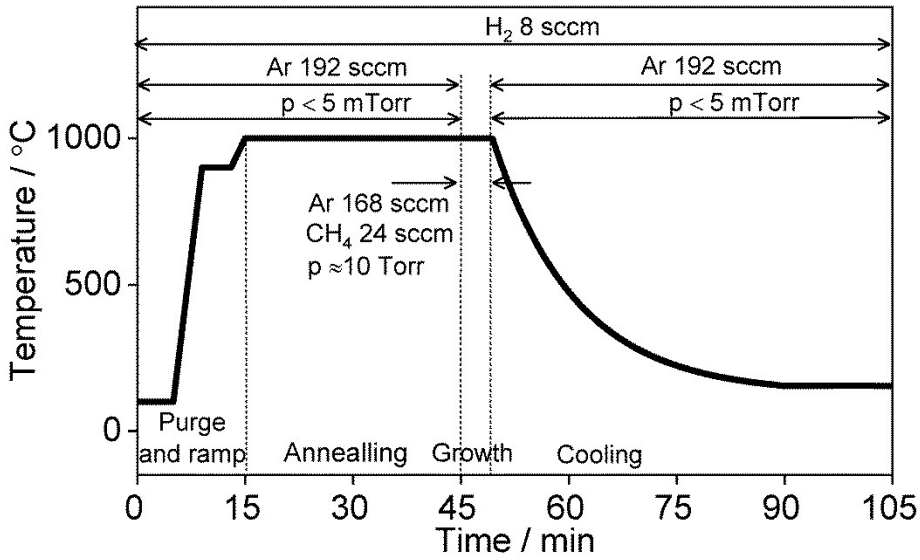

Figure S1. Synthesis parameters for chemical vapor deposition (CVD) of graphene on copper foil as the growth substrate.

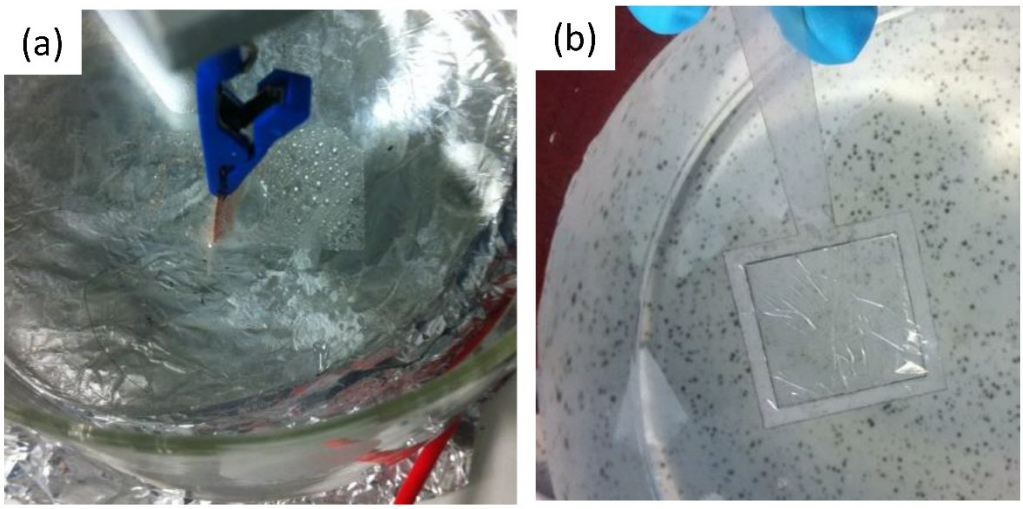

Figure S2. Photographs showing (a) delamination of graphene from copper foil by an electrochemical method and (b) an isolated graphene@PMMA film.

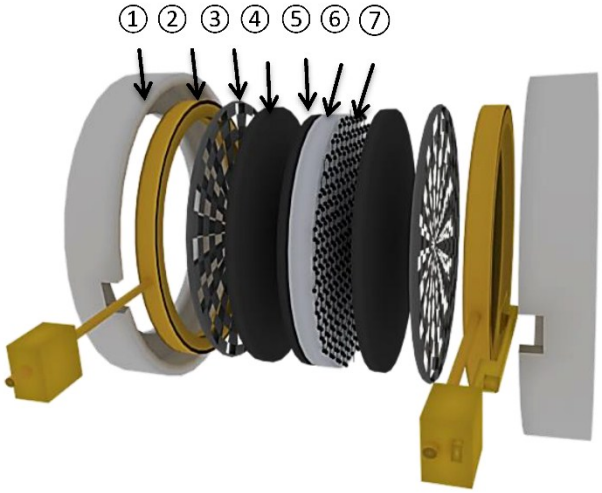

Figure S3. Schematic of the asymmetric electrochemical cell (Graphene|CDP|Pt/C/CDP) as a side view. (1) PTFE frame, (2) conducting ring, (3) gas diffusion layer, (4) carbon paper, (5) Pt/C/CDP, (6) CDP, and (7) graphene.

Table S1. ZPE and entropic corrections at T = 298.15 K

	*OH	*O	*OOH	H_2O	H_2
ZPE	0.36	0.07	0.40	0.56	0.27
TS	~	~	~	0.67	0.41

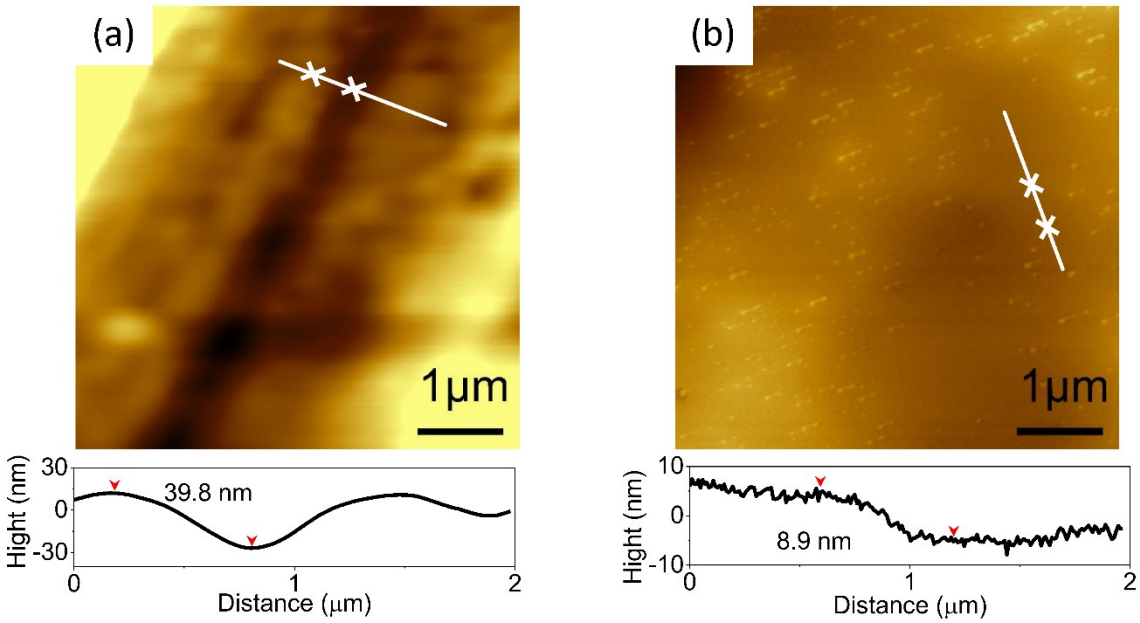

Figure S4. AFM height images of (a) pristine copper foil and (b) as-polished copper foil. Color scale: 0–150 nm.

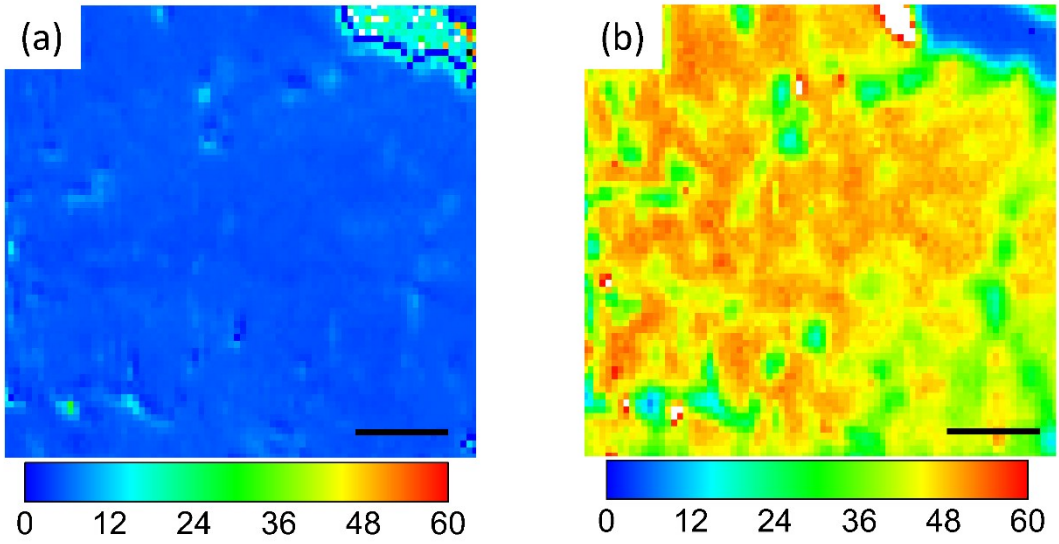

Figure S5. Raman mapping of as-transferred graphene on an SiO_2/Si substrate. Intensities of (a) G band and (b) 2D band. Scale bar = 5 μm.

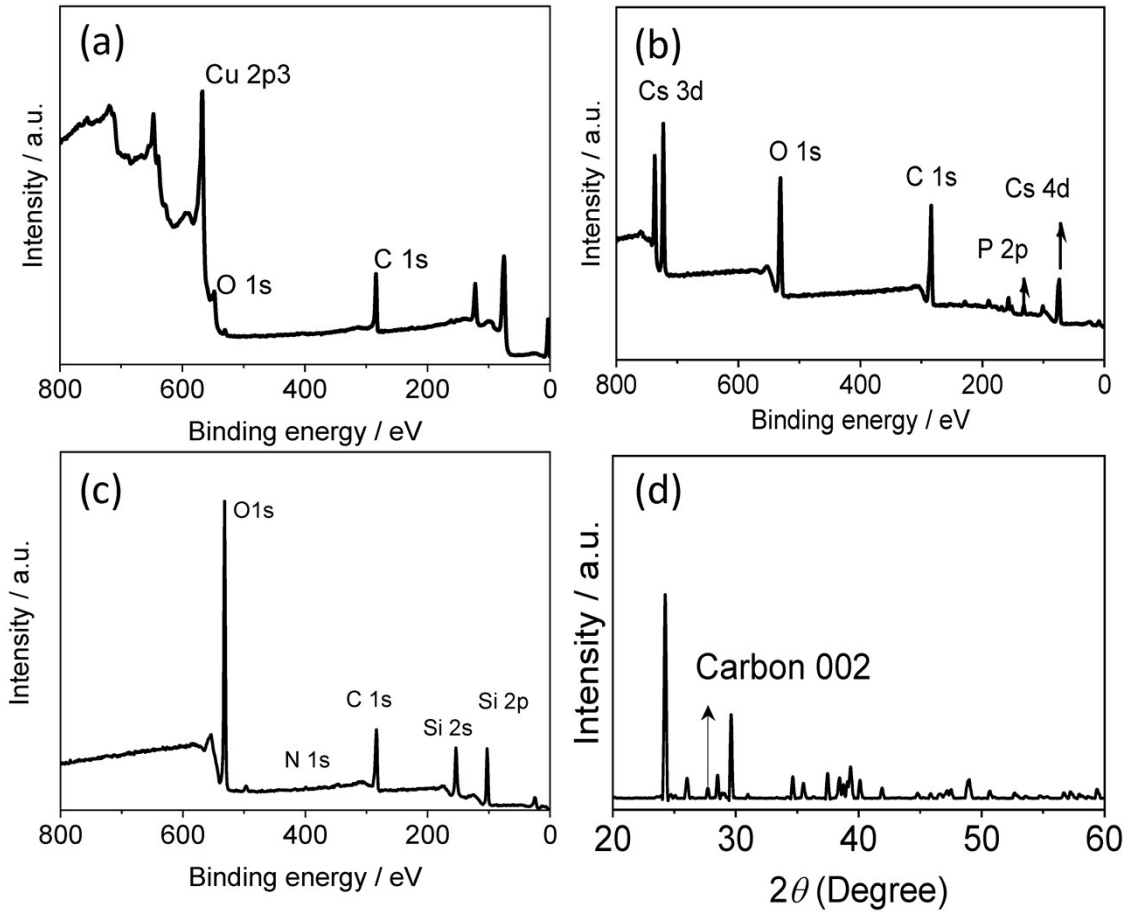

Figure S6. (a) XPS survey scan of graphene on (a) Cu substrate, (b) CDP substrate. (c) SiO_2/Si substrate. (d) XRD pattern of graphene on a CDP substrate.

Table S2. Integrated atomic concentrations of graphene on Cu, SiO_2/Si, and CDP substrates determined from XPS characterization.

	Binding energy		
	Total 284.5	Total 398.2	Total 530.6
	C 1s / %	N 1s / %	O 1s / %
Graphene on Cu	53.79	0	2.66
Graphene on SiO_2/Si	56.63	0.63	42.74
Graphene on CDP	57.58	0	30.72

Table S3. Integrated atomic concentrations of graphene on an SiO_2/Si substrate with increasing treatment time of O_2 plasma determined from XPS characterization.

	Binding energy			
	Total 284.5 eV	Total 398.2 eV	Total 530.6 eV	532.6 eV
	C 1s / %	N 1s / %	O 1s / %	C=O / %
10 s	46.81	0.61	52.58	21.94
20 s	53.03	0.67	46.30	27.05
30 s	25.37	1.35	73.28	68.07
40 s	23.02	0.89	76.09	30.16

Table S4. Integrated atomic concentrations of graphene on an SiO_2/Si substrate with increasing treatment time of N_2 plasma determined from XPS characterization.

	Binding energy			
	Total	Total	Total	
	284.5 eV	398.2 eV	530.6 eV	402.8 eV
	C 1s / %	N 1s / %	O 1s / %	g-N / %
2 min	18.93	1.16	79.91	0.42
4 min	19.69	1.09	79.32	0.26
6 min	20.02	1.41	78.58	0.60
10 min	17.33	1.77	81.10	0.89

Please note that the nitrogen content of SiO_2/Si substrate is about 0.58 ± 0.23. Thus, the decrease in nitrogen content from 2 to 4 min treatment time is within experimental error.

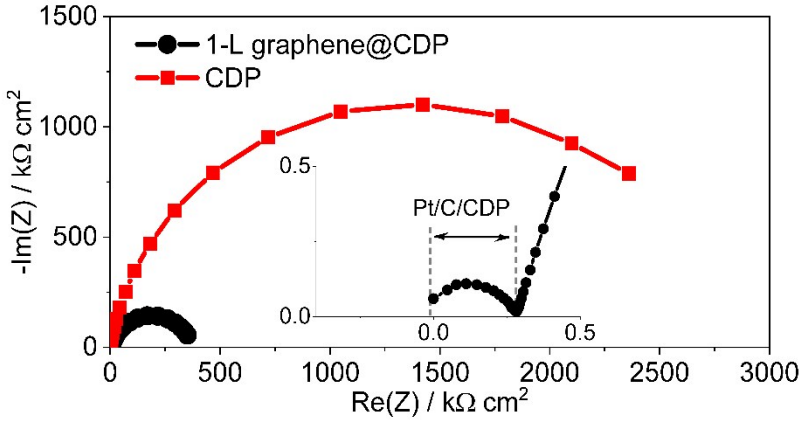

Figure S7. Impedance spectra shown as Nyquist plots for graphene|CDP|Pt/C/CDP and CDP electrochemical cells with the graphene side exposed. The measurements were performed at 240 °C in a humidified oxygen environment with a single-chamber setup.

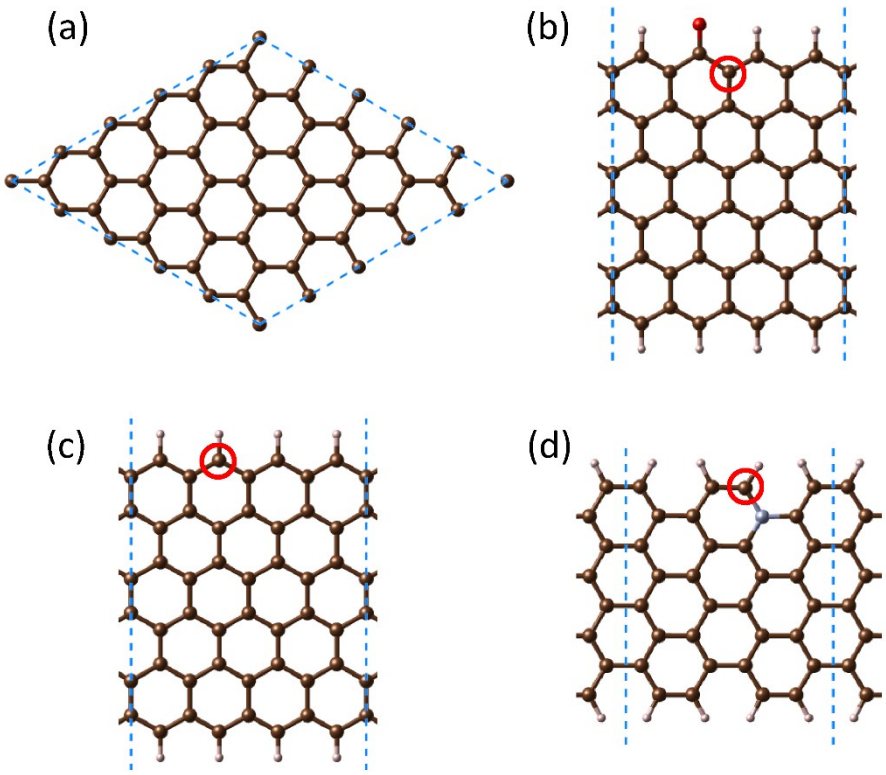

Figure S8. Atomic models and corresponding reaction sites (red circles) for (a) pristine graphene, (b) O-functionalized graphene, (c) zigzag edge of graphene, and (d) N-doped armchair edge of graphene.

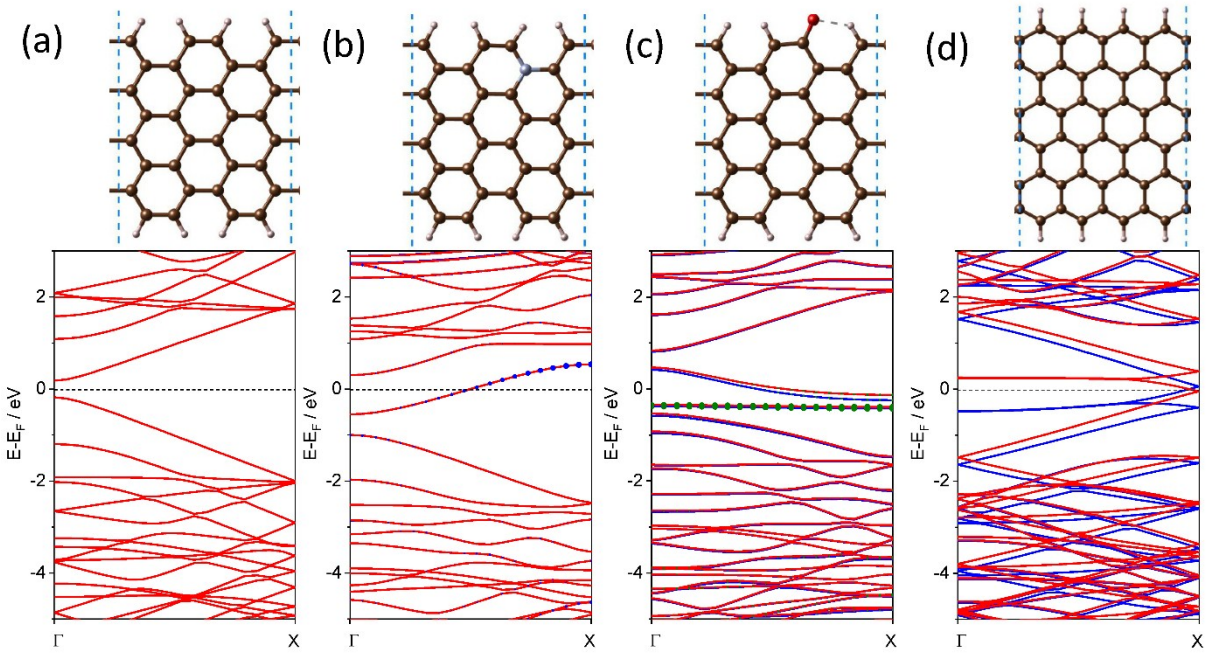

Figure S9. Electronic band structures of graphene edges with the doping of nitrogen and oxygen atoms. (a) Zigzag-edge of graphene, (b) N-doped armchair edge of graphene, (c) O-functionalized graphene, and (d) armchair-edge of graphene. Red and blue lines indicate spin-up and spin-down electronic states, respectively. The size of blue and green circles represent the relative contribution from nitrogen and oxygen atoms, respectively

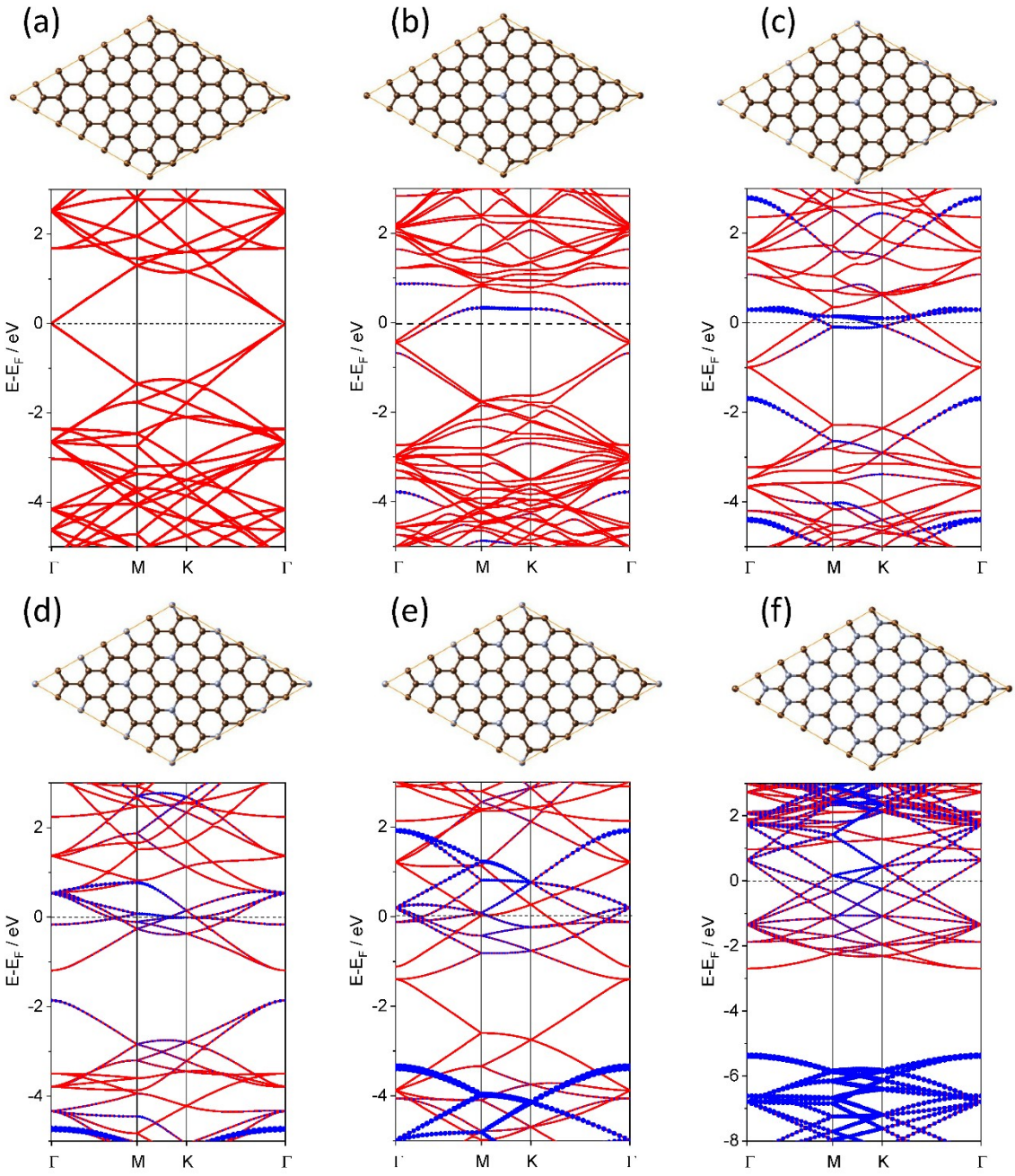

Figure S10. (a – f) Electronic band structures of periodic graphene sheets with different N concentrations. The size of blue circles represents the relative contribution from nitrogen atoms.

Table S5. Adsorption free energies (positive value) of *OH, *O, and *OOH. Armchair: AM. Zigzag: ZZ.

Models	ΔG_{*OOH} / eV	ΔG_{*O} / eV	ΔG_{*OH} / eV	Overpotential / V
Pristine	5.059	3.377	2.533	1.370
AM–edge	0.328	2.038	1.958	2.940
ZZ–edge	3.768	2.427	0.593	0.637
Pyridinic-N–AM	4.903	2.603	1.731	1.213
Graphitic-N–AM	4.029	2.116	0.879	0.351
C=O–AM	3.870	2.376	0.863	0.367

Table S6. ORR overpotential obtained from DFT calculations of oxygen plasma-treated graphene, where the adsorption free energies are positive value.

Models	ΔG_{*OOH} / eV	ΔG_{*O} / eV	ΔG_{*OH} / eV	Overpotential / V
AM-edge	0.328	2.038	1.958	2.940
ZZ-edge	3.768	2.427	0.593	0.637
C=O-AM	3.870	2.376	0.863	0.367
C=O-ZZ	5.096	2.294	2.427	1.406
C-OH-AM	4.874	1.967	1.673	1.184
C-OH-ZZ	2.621	1.576	1.606	1.259

Table S7. Adsorption energetics (positive value) and theoretical ORR overpotentials of computationally considered configurations.

Models	ΔG_{*OOH} / eV	ΔG_{*O} / eV	ΔG_{*OH} / eV	Overpotential / V
Pristine	5.059	3.377	2.533	1.370
AM-edge	0.328	2.038	1.958	2.940
ZZ-edge	3.768	2.427	0.593	0.637
Pyridinic-N-bulk	8.667	5.007	4.295	4.977
Pyridinic-N-AM	4.903	2.603	1.731	1.213
Pyridinic-N-ZZ	3.762	2.517	2.699	1.412
Pyrrolic-N–AM	5.156	0.835	1.966	2.361
Graphitic–bulk	4.533	2.696	1.308	0.843
Graphitic-N–AM	4.029	2.116	0.879	0.351
Graphitic-N–ZZ	4.992	2.160	2.261	1.331
C=O-AM	3.870	2.376	0.863	0.367
C=O-ZZ	5.096	2.294	2.427	1.406
C-OH-AM	4.874	1.967	1.673	1.184
C-OH-ZZ	2.621	1.576	1.606	1.259