Electronic Supplementary Material (ESI) for Materials Chemistry Frontiers.

Electronic Supplementary Information

Metal-free bifunctional carbon electrocatalysts derived from zeolitic imidazolate framework for efficient water splitting

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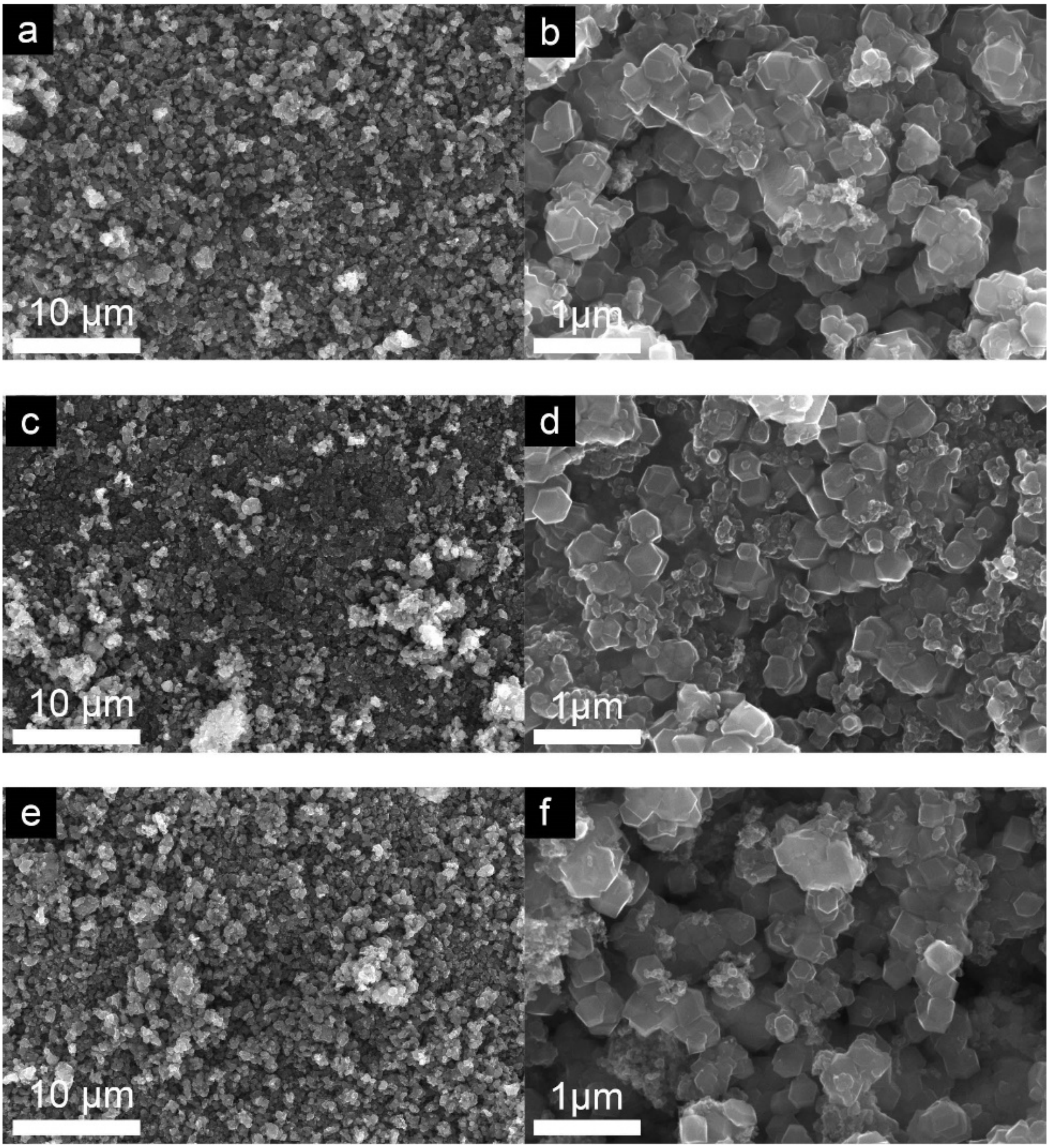

Fig. S1. SEM images of (a–b) ZiF-8-C2, (c–d) ZiF-8-C4, and (e–f) ZiF-8-C8 carbon materials at the different magnifications.

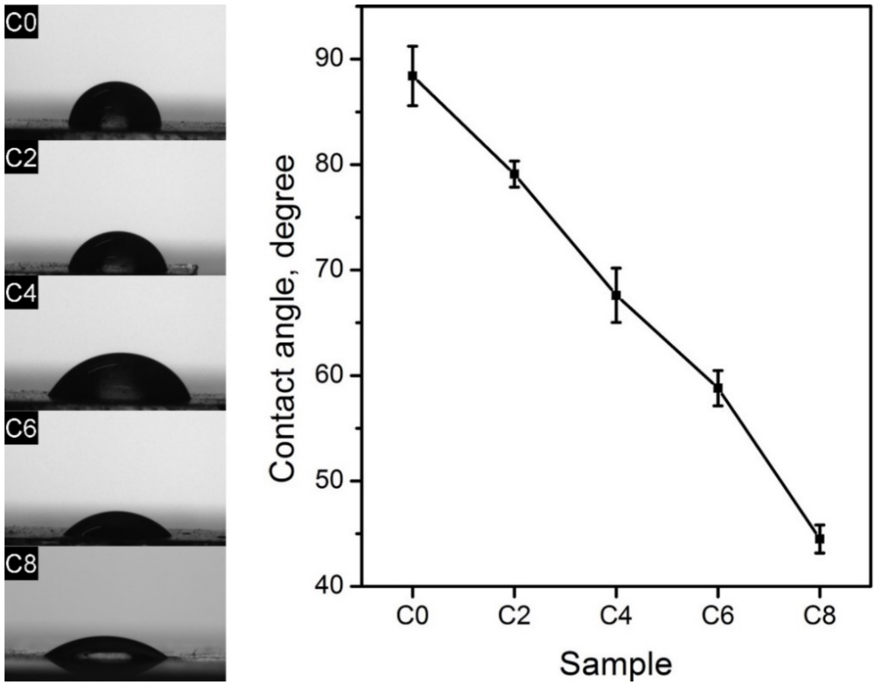

Fig. S2. Contact angle measurement of ZIF-8-C0~C8. (Left) photos and (right) contact angles.

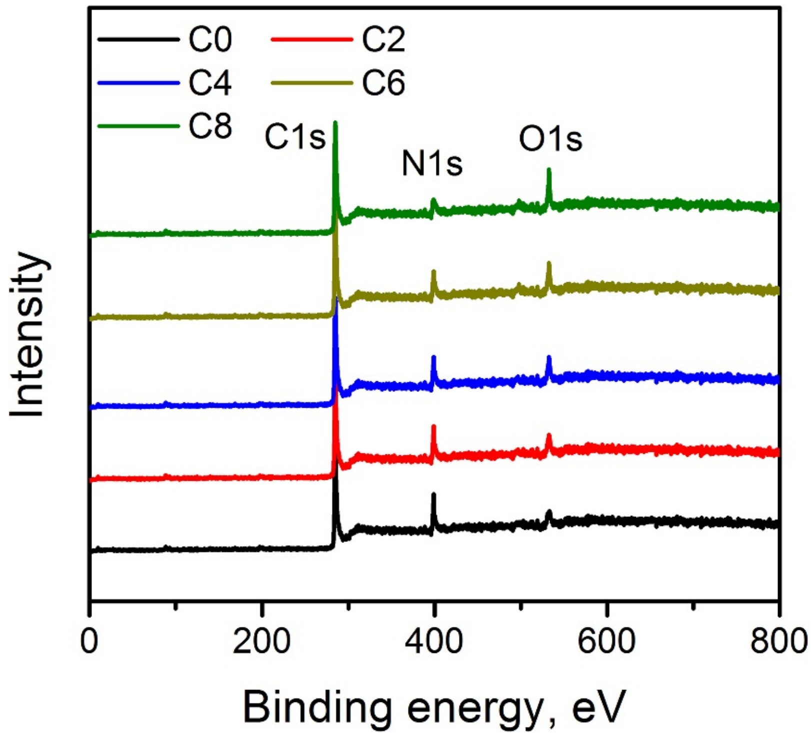

Fig. S3. XPS survey scans of ZIF-8 derived carbon materials upon the cathodic polarization treatment in 0.5 M H_2SO_4 over the different periods of time.

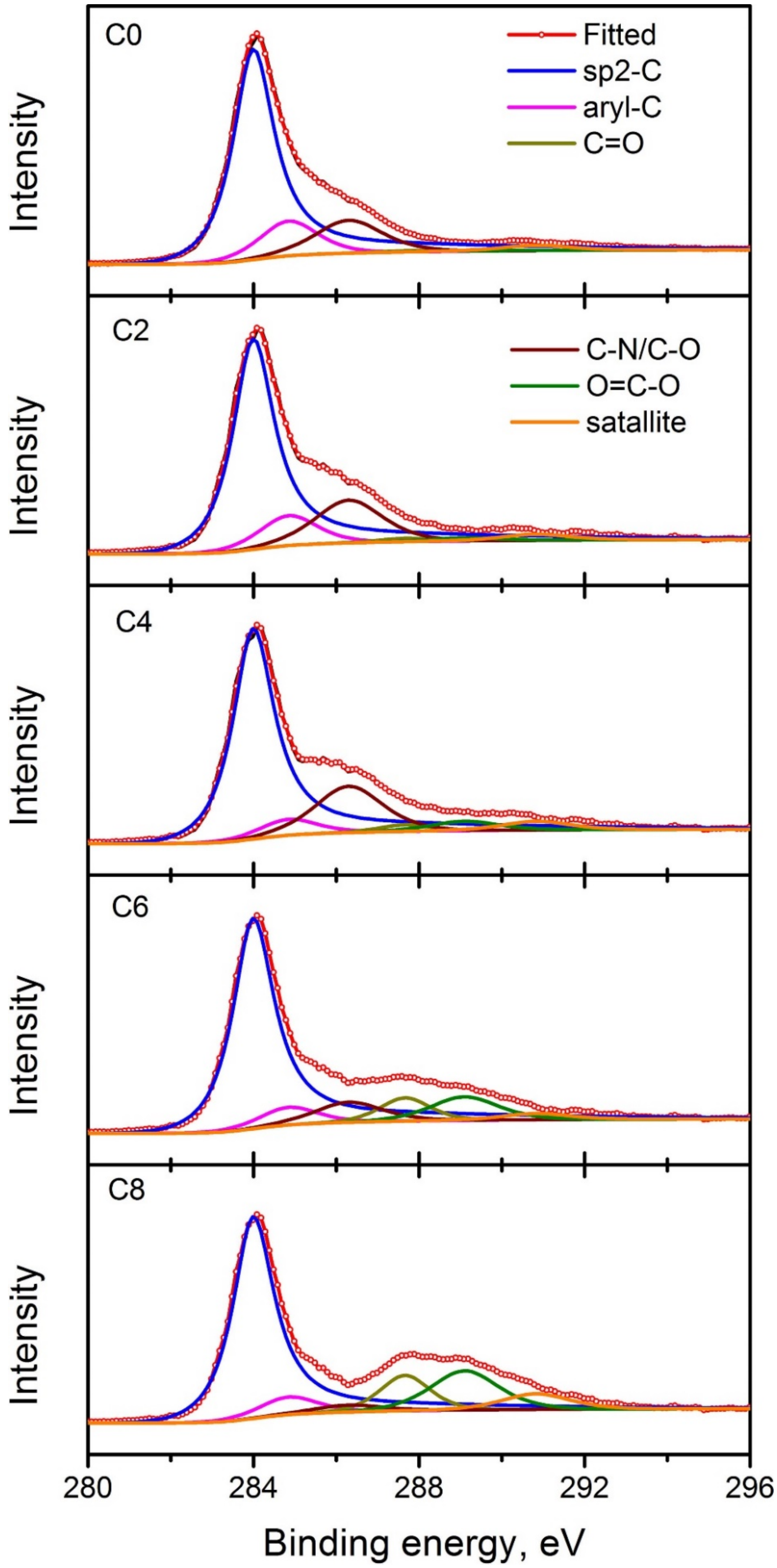

Fig. S4. Deconvolution of the high-resolution XPS spectra of C in the ZIF-8 derived carbon materials.

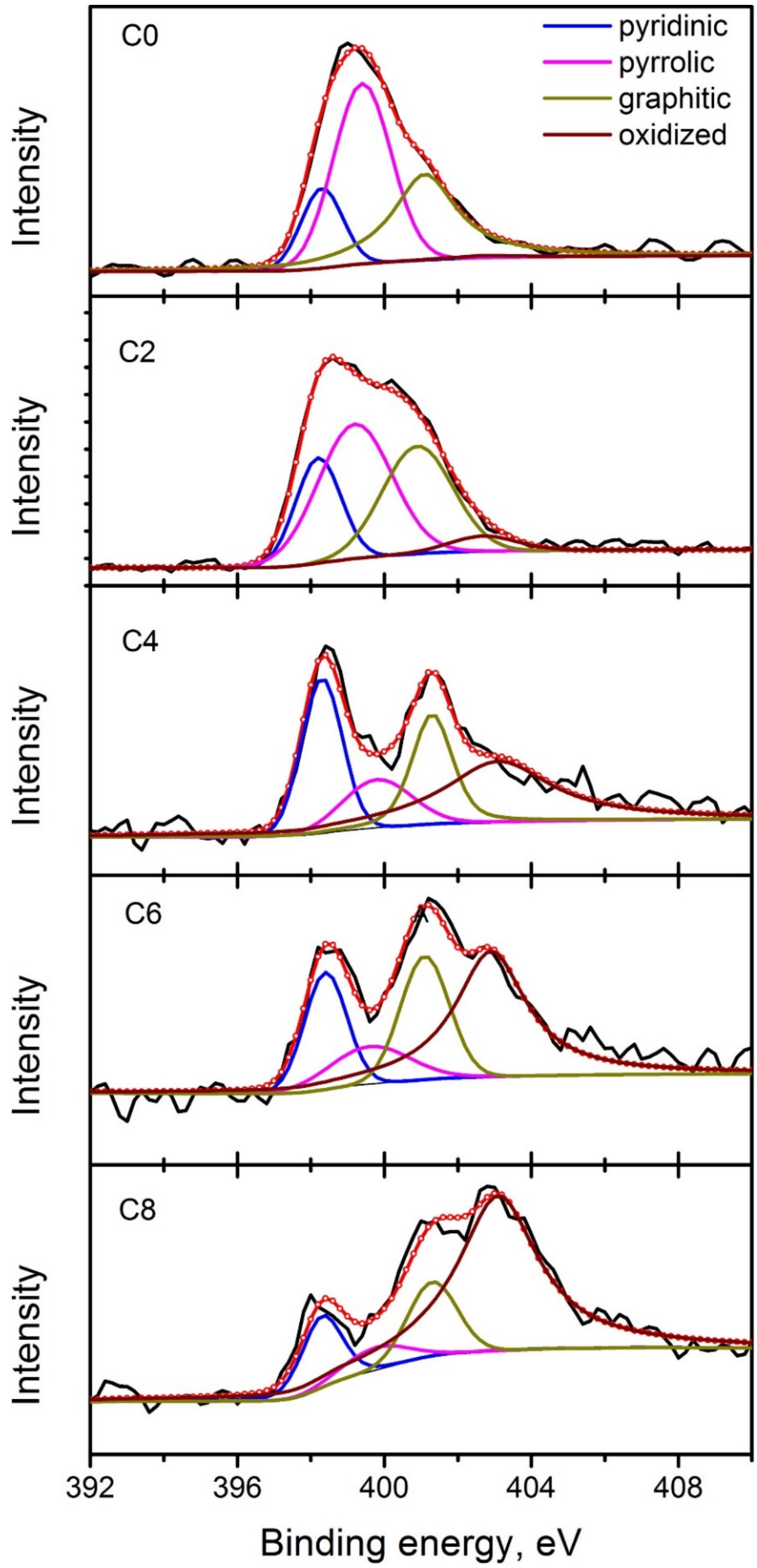

Fig. S5. Deconvolution of the high-resolution XPS spectra of N in the ZIF-8-derived carbon materials.

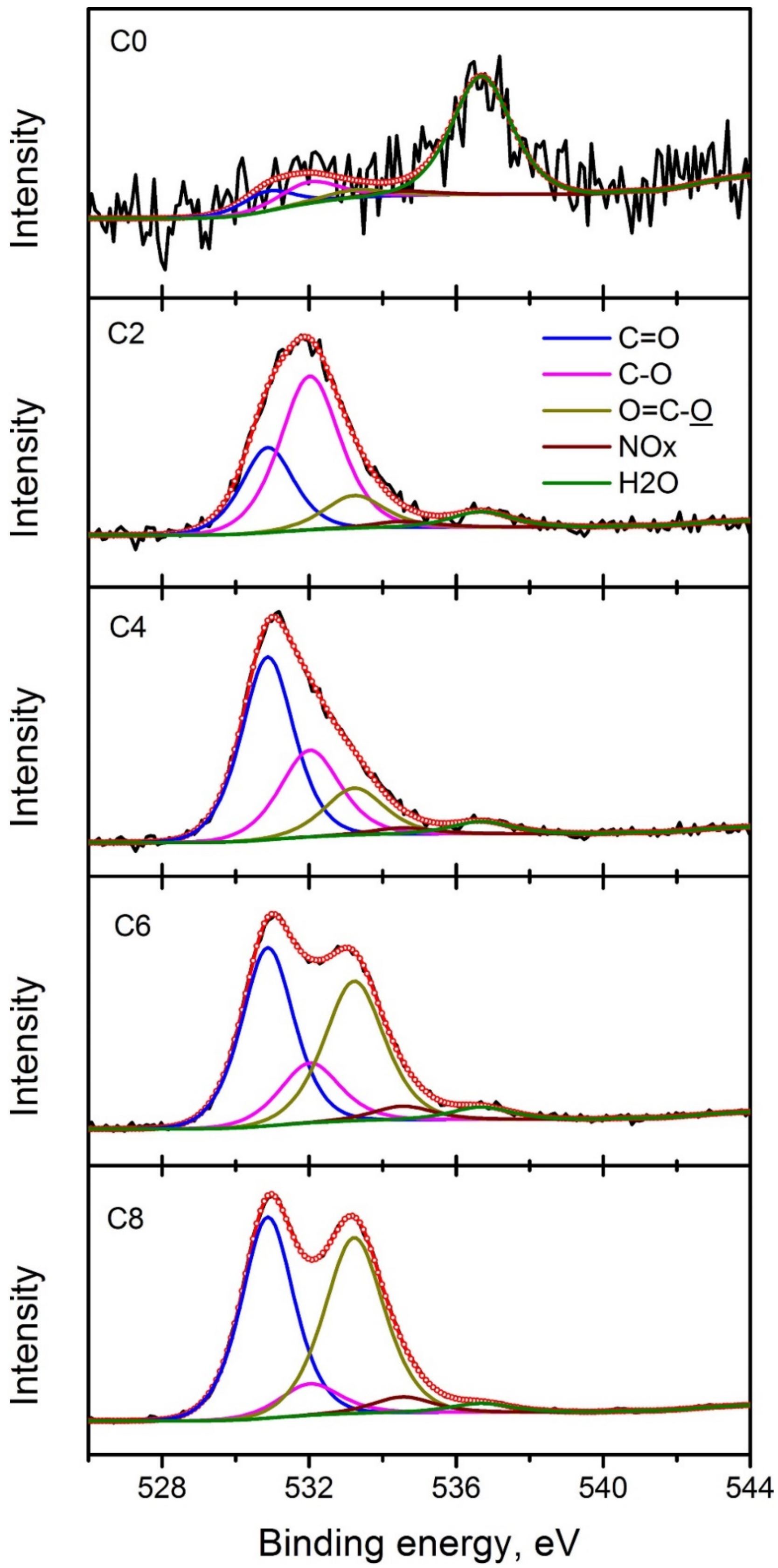

Fig. S6. Deconvolution of the high-resolution XPS spectra of O in the ZIF-8-derived carbon materials.

Table S1. Relative abundance of C, N, and O in different chemical bonds in the ZIF-8-derived carbon materials (ZIF-8-C0~C8) calculated from the deconvolution of high-resolution XPS spectra.

	ZIF-8-C	B.E., eV	Relative abundance, %				
			C0	C2	C4	C6	C8
	C in total		90.7	90.3	85.9	82.7	78.9
C	sp^2-C	283.4	75.65	73.51	72.6	71.19	64.36
	Aryl-C	284.8	12.95	10.82	7.95	6.22	9.81
	C=O	287.7	0.35	1.03	5.72	4.20	2.60
	C–N/C–O	286.2	8.56	10.82	6.12	4.92	2.60
	O=C–$\underline{O}$	289.2	0.22	1.29	4.03	10.98	14.76
	shakeup	290.8	2.26	2.53	3.58	2.50	5.88
	N in total		8.3	7.3	6.4	5.1	1.3
N	Pyridinic-	398.3	15.41	20.50	27.00	18.84	12.36
	Pyrrolic-	399.8	48.36	42.50	14.20	11.4	5.64
	Graphitic-	401.3	35.50	32.44	21.94	22.89	14.61
	Oxidized-	403.1	0.72	4.56	36.85	46.87	67.39
	O in total		1.0	2.4	7.3	12.2	19.8
O	–C=O	530.8	10.25	26.34	47.39	27.06	12.92
	C–O/–O–	532.1	12.63	54.57	9.82	6.23	5.17
	O=C–$\underline{O}$	533.3	4.69	11.58	20.84	48.48	72.00
	NO	534.6	2.48	2.04	18.34	13.96	6.34
	Chemisorbed H_2O	536.7	69.95	5.47	3.62	4.27	3.58

Table S2. Absolute atomic abundance of C, N, and O in different types of chemical bonds in ZIF-8-C0~C8 calculated from the high-resolution XPS analysis data in Table S1.

		B.E., eV	Abundance, at.%				
			C0	C2	C4	C6	C8
C	sp^2-C	283.4	68.61	66.38	62.36	58.87	50.78
	Aryl-C	284.8	11.75	9.77	6.83	5.14	7.74
	C=O	287.7	0.32	0.93	4.91	3.47	2.05
	C–N/C–O	286.2	7.76	9.77	5.26	4.07	2.05
	O=C–O	289.2	0.20	1.16	3.46	9.08	11.65
	shakeup	290.8	2.05	2.28	3.08	2.07	4.64
N	Pyridinic-	398.3	1.28	1.50	1.73	0.96	0.16
	Pyrrolic-	399.8	4.01	3.10	0.91	0.58	0.07
	Graphitic-	401.3	2.95	2.37	1.40	1.17	0.19
	Oxidized-	403.1	0.06	0.33	2.36	2.39	0.88
O	–C=O	530.8	0.10	0.63	3.46	3.30	2.56
	C–O/–O–	532.1	0.13	1.31	0.72	0.76	1.02
	O=C–O	533.3	0.05	0.28	1.52	5.91	14.26
	NO	534.6	0.02	0.05	1.34	1.70	1.26
	Chemisorbed H_2O	536.7	0.70	0.13	0.26	0.52	0.71

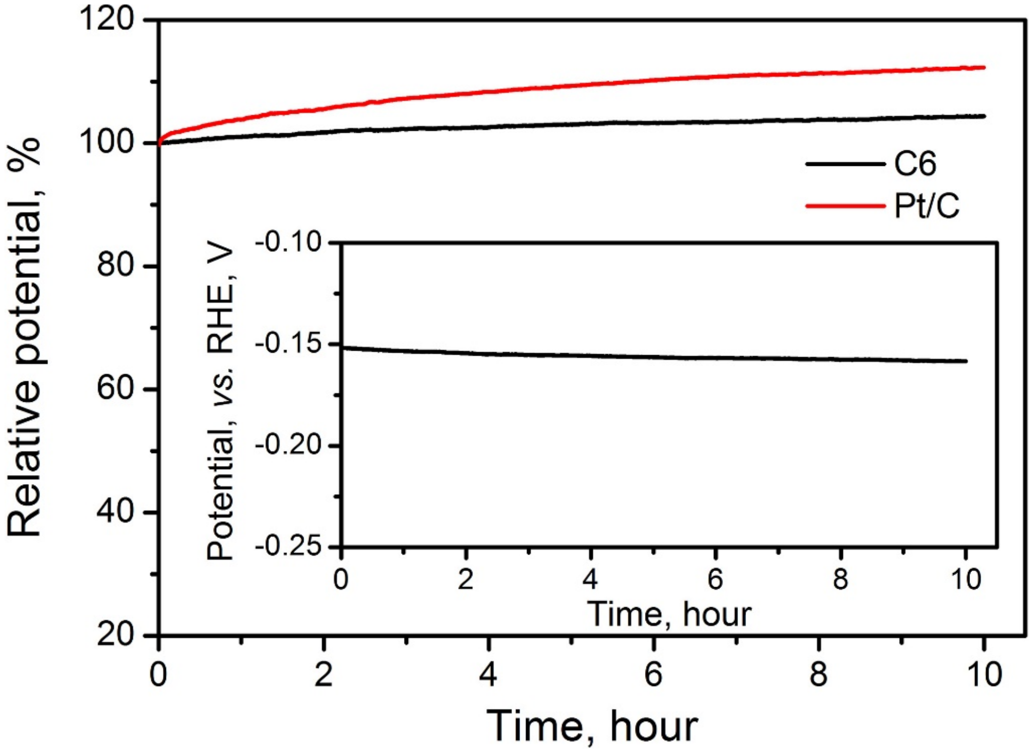

Fig. S7. The relative potentials of ZIF-8-C6 and Pt/C electrocatalysts in the HER tests carried out at 10 mA/cm^2 in 0.5 M H_2SO_4 electrolyte for 10 hours. The inset shows the chronoamperometric curve of ZIF-8-C6.

Table S3. Comparison of HER performance of recently reported metal-free carbon electrocatalysts in 0.5 M H_2SO_4.

Carbon catalyst	Tafel slope, mV/dec	η_{10}, mV	loading, mg/cm^2	j_0, mA/cm^2	Ref.
ZIF-8-C6	54.7	155	0.3	6.3×10^{-2}	*This work*
N,P-graphene	91.0	420	0.2	2.4×10^{-4}	*ACS Nano* **2014**, 8, 5290
N,S-graphene	81	276	N/A	8.4×10^{-3}	Angew. Chem. Int. Ed., **2015**, 54, 2131
C_3N_4@NG	51.5	240	0.1	3.5×10^{-4}	Nat. Commun., **2014**, 5, 3783
C_3N_4@G	54	207	0.14	4.0×10^{-2}	Angew. Chem. Int. Ed., **2014**, 53, 13934
C3N4@N-graphene-750	49.1	80	N/A	4.3×10^{-1}	ACS Nano, **2015**, 9, 931
p-MWCNT-ao-cp	71.3	N/A	N/A	1.6×10^{-3}	Chem. Commun., **2014**, 50, 9340
N,S-carbon	80.5	290	N/A	N/A	Angew. Chem. Int. Ed., **2015**, 54, 2131
$C_{60}(OH)_8$	78	N/A	0.002	7×10^{-4}	Angew. Chem. Int. Ed., **2013**, 52, 10867
N-carbon	109	239	N/A	N/A	Sci. Rep., **2014**, 4, 7557
N,P-bacteria-derived carbon	58.4	204	0.152	1.7×10^{-2}	J. Mater. Chem. A, **2015**, 3, 7210
B-carbon	99	310	N/A	N/A	Catal. Sci. Technol., **2014**, 4, 2023
NSC/MPA-5	99	240	0.25	4.810^{-3}	Nano Energy, **2017**, 32, 336
N,S-CNT	67.8	120	0.285	N/A	Nano Energy, **2015**, 16, 357
N,S-carbon	57.4	97	0.285	N/A	J. Mater. Chem. A, **2015**, 3, 8840
N,P-carbon	79	213	0.2	2.43×10^{-2}	J. Mater. Chem. A, **2015**, 3, 12642
N-rich holey	157	510	0.216	6.38×10^{-3}	Nano Energy, **2015**,

graphene (N-G)					15, 567
C_3N_4@S,Se-G	86	300	0.283	6.27×10^{-3}	J. Mater. Chem. A, **2015**, 3, 12810

Table S3. Comparison of HER performance of recently reported metal-free carbon electrocatalysts in 0.1 M KOH.

Carbon catalyst	Tafel slope, mV/dec	η_{10}, mV	Ref.
C6	97.4	336	*This work*
SHG	112	310	Adv. Mater., **2017**, 29, 1604942
N-rich holey graphene (N-G)	157	510	Nano Energy, **2015**, 15, 567
N,P-G	N/A	>600	ACS Nano, **2014**, 8, 5290
N,P-C	N/A	470	Angew. Chem. Int. Ed., **2016**, 128, 2270
N,O,P-G	154	450	Energy Environ. Sci., **2016**, 9, 1210
C_3N_4@N-G	N/A	>600	Nat. Commun., **2014**, 5, 3783
C_3N_4@S,Se-G	93	1100	J. Mater. Chem. A, **2015**, 3, 12810
C_3N_4@N,P-G	129	580	ChemCatChem, **2015**, 7, 3873

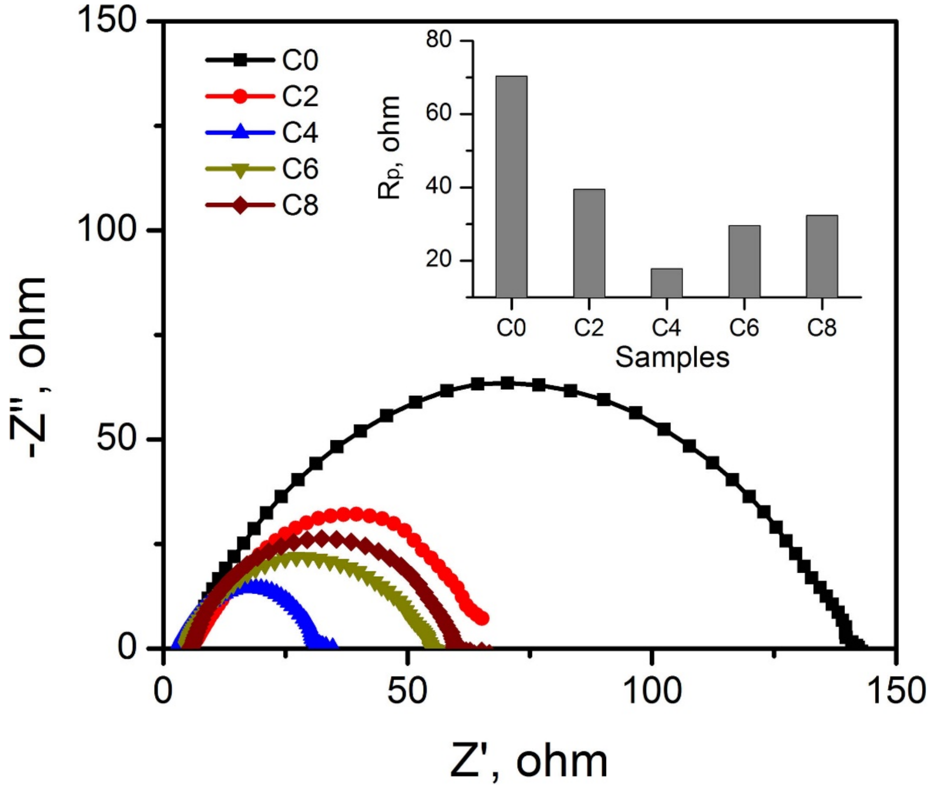

Fig. S8. EIS Nyquist plots of the ZIF-8-derived electrocarbocatalysts for OER in 0.1 M KOH electrolyte. All plots are recorded with the overpotential of 0.3 V. The insert shows the polarization resistance (R_P).

Table S5. Comparison of OER performance of recently reported metal-free carbon electrocatalysts in 0.1 M KOH.

Catalyst	Electrolyte	Tafel slope, mV/dec	η_{10}, mV	Ref.
ZIF-8-C4	0.1 M KOH	78.5	476	*This work*
N, S co-doped graphitic sheets with holes	0.1 M KOH	71	370	Adv. Mater., **2017**, 29, 1604942
N-carbon film	0.1 M KOH	128	190	Adv. Sci., **2015**, 2, 1400015
N-doped CNT	0.1 M KOH	383	450	ACS Appl. Mater. Interfaces, **2015**, 7, 11991
N-doped graphite	0.1 M KOH	N/A	380	Nat. Commun., **2013**, 4, 2390
N-doped carbon	0.1 M KOH	N/A	390	Carbon, **2013**, 53, 130
Oxidized carbon cloth	0.1 M KOH	82	490	Chem. Comm., **2015**, 51, 1616
N,P-graphene	0.1 M KOH	70	340	ACS Catal., **2015**, 5, 4133
N,O-carbon hydrogel	0.1 M KOH	141	400	Adv. Mater., **2014**, 26, 2925
N,P-G	0.1 M KOH	59	420	Nano Energy, **2016**, 19, 373
N,O,P-G	0.1 M KOH	84	400	Energy Environ. Sci., **2016**, 9, 1210
g-C_3N_4/G	0.1 M KOH	68.5	580	ChemSusChem, **2014**, 7, 2125
N-G/CNT	0.1 M KOH	97	510	Small, **2014**, 10, 2251
N-GRW	0.1 M KOH	62	440	Sci. Adv., **2016**, 2, e1501122
Surface oxidized MWCNT	0.1 M KOH	72	450	J. Am. Chem. Soc, **2015**, 137, 2901
P-C_3N_4	0.1 M KOH	61.6	400	Angew. Chem, Int. Ed., **2015**, 54, 4650
g-C_3N_4-CNT	0.1 M KOH	83	350	Angew. Chem. Int. Ed., **2014**, 53, 7281
N-Carbon nanocable	0.1 M KOH		520	Adv. Funct. Mater., **2014**, 24, 5956

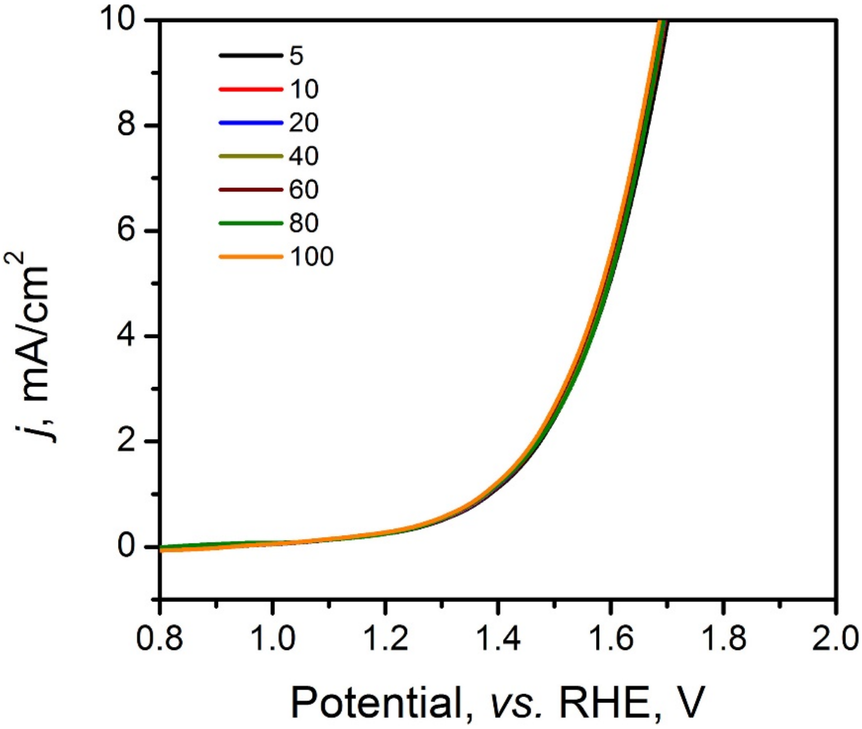

Fig. S9. OER LSV curve of ZiF-8-C4 obtained at the different scan rates (from 5 to 100 mV/s) in 0.1 M KOH electrolyte.

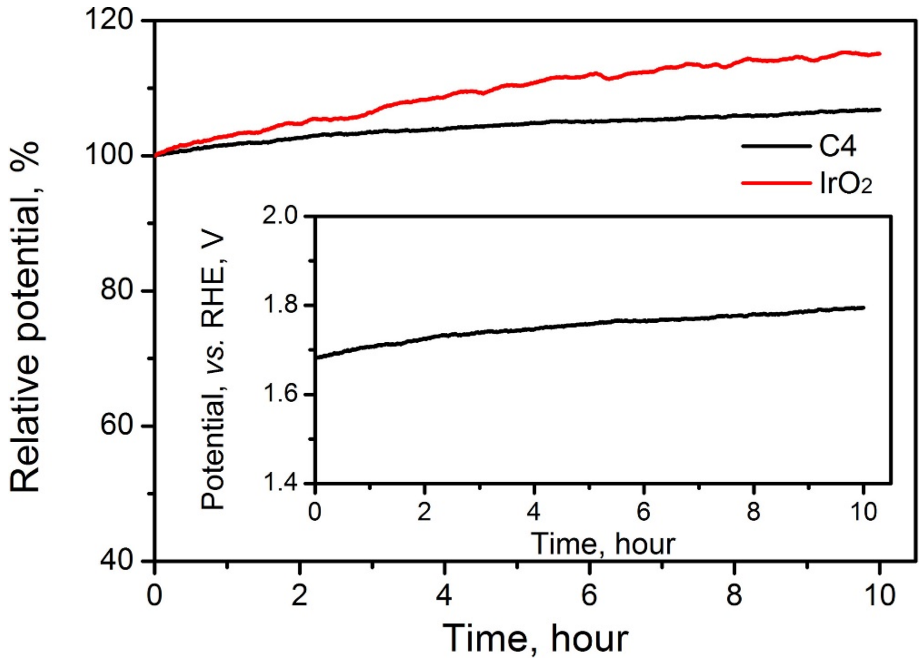

Fig. S10. The relative potentials of ZIF-8-C4 and IrO_2 catalysts in the OER tests carried out at 10 mA/cm^2 in 0.1 M KOH electrolyte for 10 hours. The inset shows the chronoamperometric curve of ZIF-8-C4.

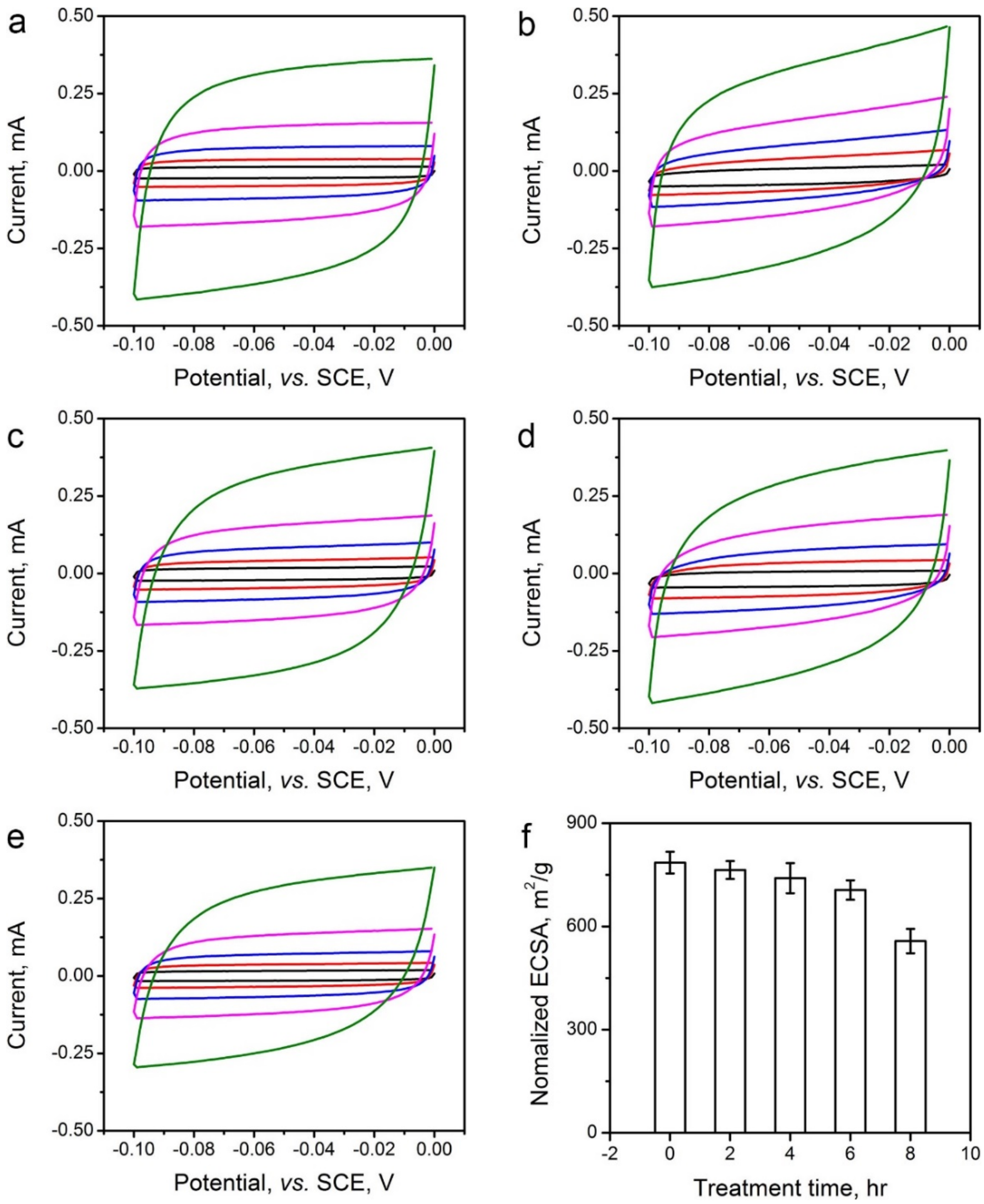

Fig. S11. Cyclic voltammetry (CV) scan curves of ZIF-8-C0~C8. The scan rates vary from 5 to 50 mV/s. (f) The calculated ECSA values for ZIF-8-C0~C8.

Electrochemical active surface area (ECSA) of ZIF-8-C0~C8 is determined by measuring the double layer capacitance (C_{dl}) of ZIF-8-C0~C8 in a non-Faradaic region (–0.1 to 0 V *vs.* SCE) and normalized by the specific capacitance of carbon surface, which is 20 mF/cm^2. C_{dl} value is calculated from the cyclic voltammetry scans performed from 5 to 50 mV/s.

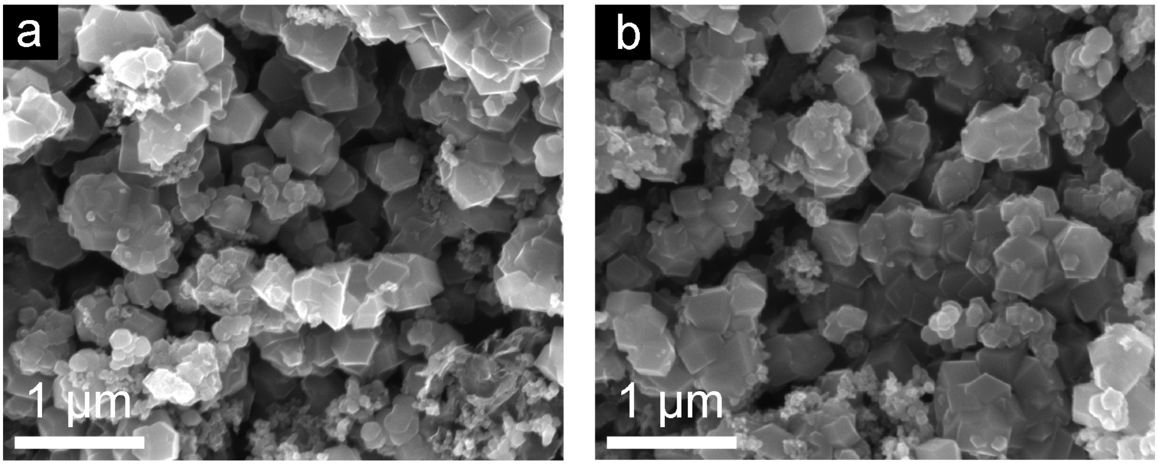

Fig. S12. SEM images of (a) ZiF-8-C4 and (b) ZiF-8-C6 after the 8-hour electrolysis test in 0.1 M KOH.

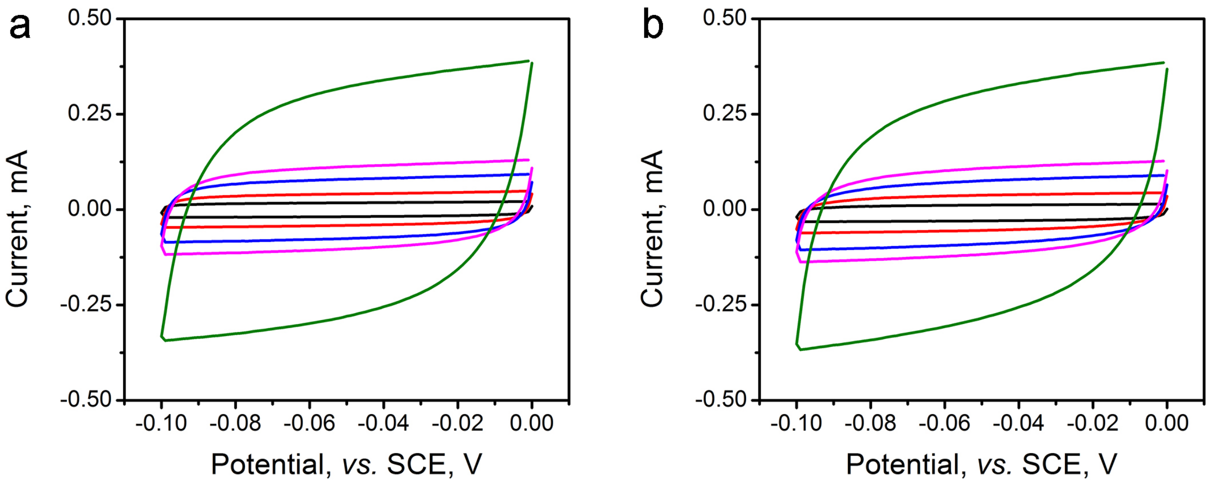

Fig. S13. ECSA measurements of (a) ZiF-8-C4 and (b) ZiF-8-C6 after the 8-hour electrolysis test in 0.1 M KOH.