Electronic Supplementary Information

Electrocatalysis for Oxygen Reduction Reaction on EDTAFeNa and Melamine co-Derived self-Supported Fe-N-C materials

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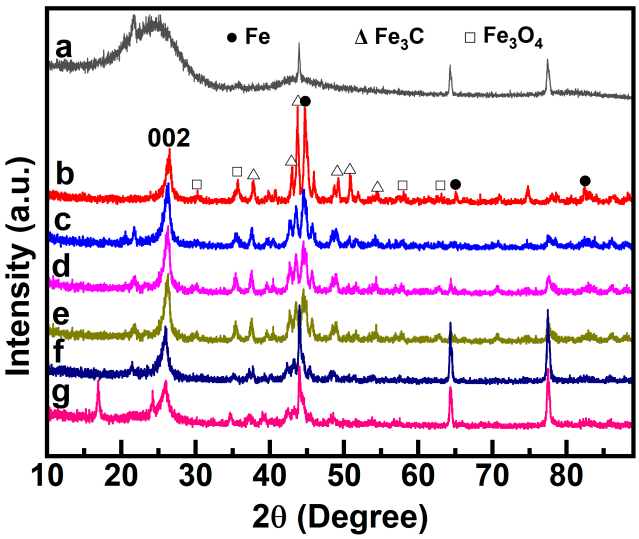

Figure S1. XRD patterns of the MA/EDTA-HT2 (a) and MA/EDTAFeNa-HT2 prepared under 0.5 h (b), 1 h (c) and 2 h (d) of acid-leaching time, and mass ratio of MA/EDTAFeNa of 2:4 (e), 3:4 (f) and 4:4 (g), respectively.

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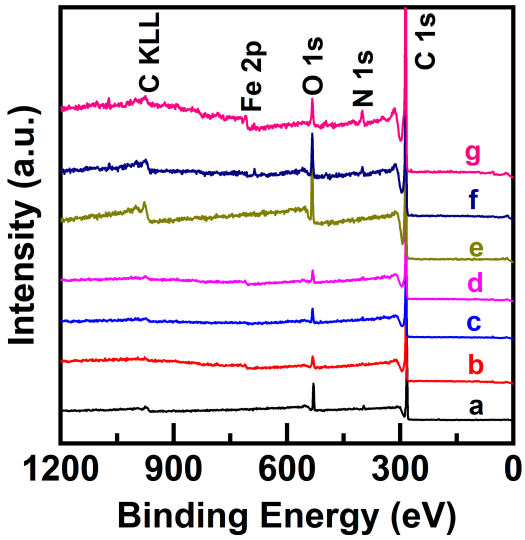

Figure S2. XPS survey spectra of the MA/EDTA-HT2 (a) and MA/EDTAFeNa-HT2 prepared under 0.5 h (b), 1 h (c) and 2 h (d) of acid-leaching time, and mass ratio of MA/EDTAFeNa of 2:4 (e), 3:4 (f) and 4:4 (g), respectively.

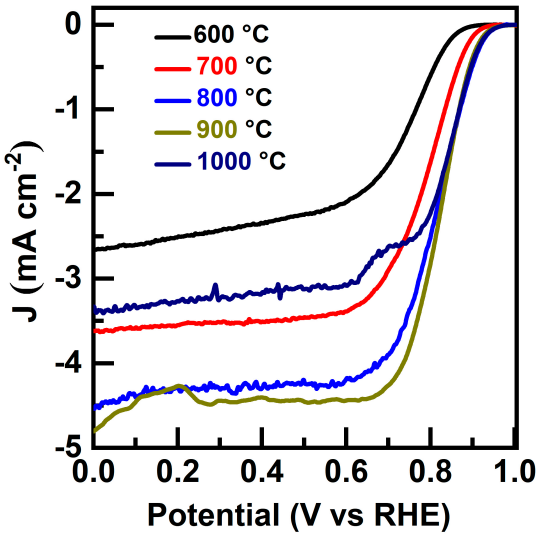

Figure S3. LSV curves for ORR on the MA/EDTAFeNa-HT2 prepared under different pyrolysis temperature (HT2), respectively.

Table S1. Surface chemical compositions and atomic concentration of the series of MA/EDTAFeNa-HT2

Sample	N	C	Fe	O
	at%			
MA/EDTA-HT2	1.56	88.03	0.09	10.32
MA/EDTAFeNa-HT2(AL0.5 h)	1.13	93.39	1.15	4.34
MA/EDTAFeNa-HT2(AL1 h)	0.70	94.37	0.27	4.65
MA/EDTAFeNa-HT2(AL2 h)	1.23	94.35	0.94	3.48
MA/EDTAFeNa-HT2(600 ℃)	0.56	91.96	0.92	6.56
MA/EDTAFeNa-HT2(700 ℃)	1.60	92.43	0.59	5.38
=0.56MA/EDTAFeNa-HT2(800 ℃)	1.15	93.98	0.73	4.15
MA/EDTAFeNa-HT2(1000 ℃)	2.67	92.00	0.24	5.08
MA/EDTAFeNa-HT2(2:4)	1.48	84.91	0.51	13.11
MA/EDTAFeNa-HT2(3:4)	3.41	88.17	0.53	7.89
MA/EDTAFeNa-HT2(4:4)	4.41	89.86	1.01	4.72

* Determined by XPS elemental analysis

Table S2. Atomic concentration of varied N configurations in the series of MA/EDTAFeNa-HT2

Sample	Pyridinic N	Pyrrolic N	Graphitic /quaternary N	Oxidized pyridinic N
	at%			
MA/EDTA-HT2	0.16	0	1.40	0
MA/EDTAFeNa-HT2(AL0.5 h)	0.16	0.64	0.12	0.21
MA/EDTAFeNa-HT2(AL1 h)	0.11	0.39	0.08	0.13
MA/EDTAFeNa-HT2(AL2 h)	0.19	0.33	0.20	0.51
MA/EDTAFeNa-HT2(600 ℃)	0.12	0.26	0.04	0.13
MA/EDTAFeNa-HT2(700 ℃)	0.29	0.72	0.34	0.25
MA/EDTAFeNa-HT2(800 ℃)	0.29	0.24	0.36	0.26

MA/EDTAFeNa-HT2(1000 ℃)	0.42	1.23	0.24	0.77
MA/EDTAFeNa-HT2(2:4)	0.29	0.47	0.52	0.20
MA/EDTAFeNa-HT2(3:4)	0.52	1.16	1.28	0.46
MA/EDTAFeNa-HT2(4:4)	0.33	2.34	0.85	0.89

* Determined by XPS elemental analysis

The number of transferred electrons and kinetic current density in the ORR can be calculated from Koutecky-Levich (K-L) equation [1,2]:

(1) $J^{-1} = J_L^{-1} + \boldsymbol{J_k}^{-1} = (B\omega^{1/2})^{-1} + \boldsymbol{J_k}^{-1}$

(2) $B = 0.20\, \boldsymbol{n}FC_0(D_0)^{2/3}v^{-1/6}$

(3) $\boldsymbol{J_k} = \boldsymbol{n}FkC_0$

where J is the measured current density, J_L and $\boldsymbol{J_k}$ is the diffusion-limiting and kinetic current density, ω is the electrode rotation speed (rpm), $\boldsymbol{n}$ is the number of transferred electrons required on the average for the reduction of an oxygen molecule, F is the Faraday constant (F = 96485 C mol^{-1}), C_0 and D_0 are the bulk concentration and diffusion coefficient of O_2 ($C_0 = 1.2\times10^{-3}$ mol/L, $D_0 = 1.9\times10^{-5}$ cm^2 s^{-1}), respectively, v is the kinematic viscosity of the electrolyte (v = 0.01 cm^2 s^{-1}), and k is the electron-transfer rate constant. According to equations (1) and (2), the $\boldsymbol{n}$ and $\boldsymbol{J_k}$ can be obtained from the slope and intercept of the Koutecky-Levich plots, respectively.

References

[1] Bard, A.J.; Faulkner, L.R. Electrochemical methods: fundamentals and applications 2nd edition, Wiley New York, **2000**.

[2] Yang, S.B.; Feng, X.L.; Wang, X.C.; Müllen, K. Graphene-based carbon nitride nanosheets as efficient metal-free electrocatalysts for oxygen reduction reactions. *Angew. Chem. Int. Ed.* **2011**, 50: 5339-5343.