Single-atom Catalysts with Hollow Rod/Plate like Structure for Enhanced Oxygen Reduction Reaction Performance in Zinc Air Battery

*Muhammad Arif Khan[1, a], Guopu Cai[1, b], Rida Javed [d], Daixin Ye [c, *], and Hongbin Zhao[b,*], and Jiujun Zhang [c]*

a School of Materials Science and Engineering, Shanghai University, Shanghai 200444, PR China;

b Department of Chemistry, College of Sciences, Shanghai University, Shanghai 200444, PR China;

c College of Sciences &Institute for Sustainable Energy, Shanghai University, Shanghai 200444, PR China;

d College of Materials science and Engineering, Shenzhen university, Shenzhen, Guangdong, PR China;

Experimental

Synthesis of Co-N-C SAC

Cobalt hydroxide nanoplates $Co(OH)_2$) were synthesized through hydrothermal method. In an experiment, 60 ml of DI water was taken in a beaker and 2.18 g of $CoCl_2.6H_2O$ was dissolved in it through ultra-sonication for 3 minutes. After that 3 ml of the $N(CH_2CH_3)_3$ was added to the above solution and stirred for 2 h. It was then transferred to 100 ml Teflon vessel and hydrothermal treatment was done at 180^{o}C for 24 h. The pink precipitate obtained after centrifugation with ethanol and DI water followed by drying at 80^{o}C on oven is named as $Co(OH)_2$ nanoplates.

In the second step, 300 mg of $Co(OH)_2$ nanoplates and 15 mg of SDS were dispersed in 100 ml of DI water through stirring at room temperature for 4 h. Aniline monomer (90 µL), 1 ml H_2SO_4 solution (0.1 M), and 250 mg of APS were added to the above solution

and stirred for 2 h to complete the aniline polymerization. A black precipitate was obtained through centrifugation with DI water and ethanol followed by drying at 80^{o}C. Co-N-C SAC was obtained after pyrolysis at 500^{o}C for 2 h followed by acid leaching.

Synthesis of Ni-N-C SAC

Nickel hydroxide nanoplates $Ni(OH)_2$) were synthesized through hydrothermal method. In an experiment, 60 ml of DI water was taken in a beaker and 1.98 g of $NiCl_2.6H_2O$ was dissolved in it through ultra-sonication for 3 minutes. After that 3 ml of the $N(CH_2CH_3)_3$ was added to the above solution and stirred for 2 h. It was then transferred to 100 ml Teflon vessel and hydrothermal treatment was done at 170^{o}C for 24 h. The green precipitate obtained after centrifugation with ethanol and DI water followed by drying at 80^{o}C on oven is named as $Ni(OH)_2$ nanoplates.

The Ni-N-C SAC formation process is same as explained for Co-N-C SAC.

Synthesis of Mn-N-C SAC

Hydrothermal method was used to synthesize Manganese oxide (MnO_2) nanorods. In an experiment, 1.69 g of $MnSO_4.H_2O$, 0.275 g of $(NH_4)_2S_2O_8$, and 0.315 g of $(NH_4)_2S_2O_8$ were added in 60 ml of DI water and stirred for 3 h. This solution was hydrothermally treated at 160^{o}C for 16 h. The black precipitate obtained after centrifugation with ethanol and DI water followed by drying at 80^{o}C is named as MnO_2 nanorods.

The synthesis process for Mn-N-C SAC is same as described for Co-N-C SAC.

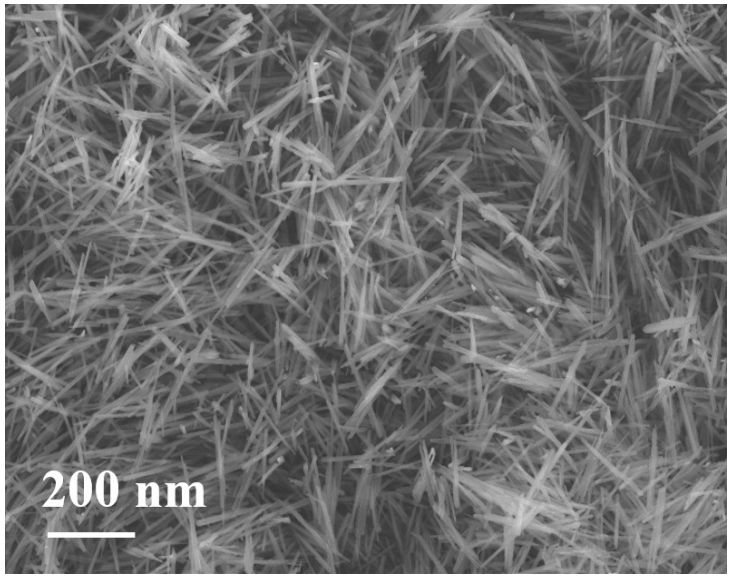

Fig. S1. SEM image for FeOOH.

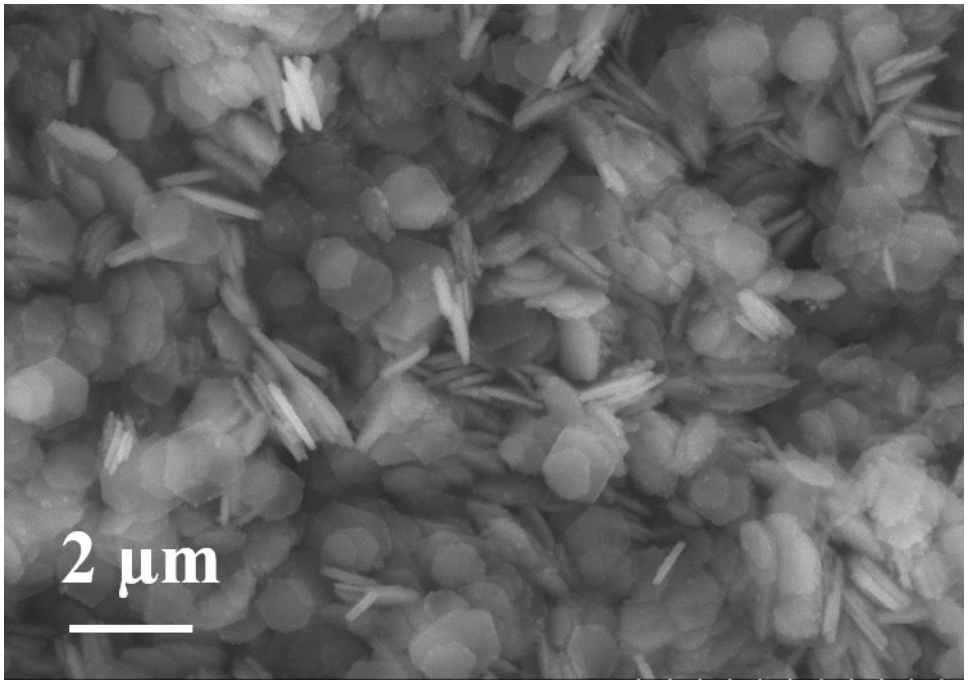

Fig. S2. SEM of $Co(OH)_2$.

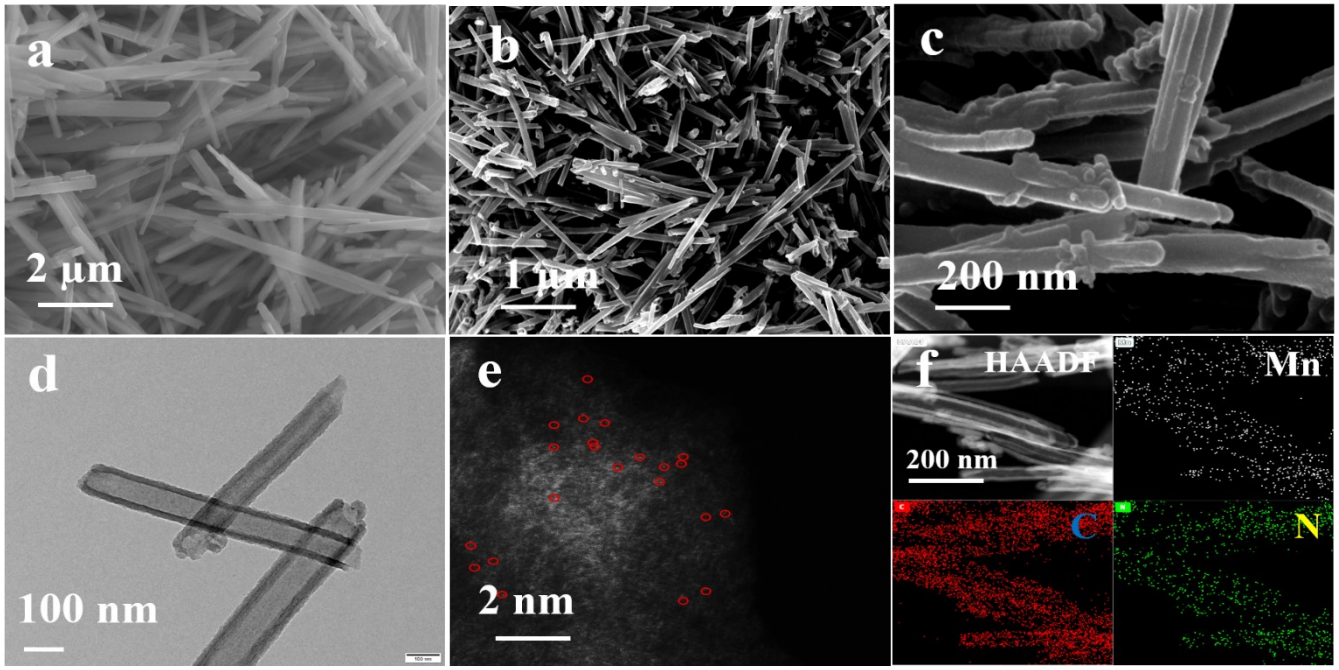

Fig. S3. (a) SEM of MnO_2; (b,c) SEM of Mn-N-C SAC; (d) TEM of Mn-N-C SAC; (e) Aberration corrected HAADF-STEM image of Mn-N-C SAC; (f) HAADF-STEM image and corresponding EDX mapping of Mn-N-C SAC.

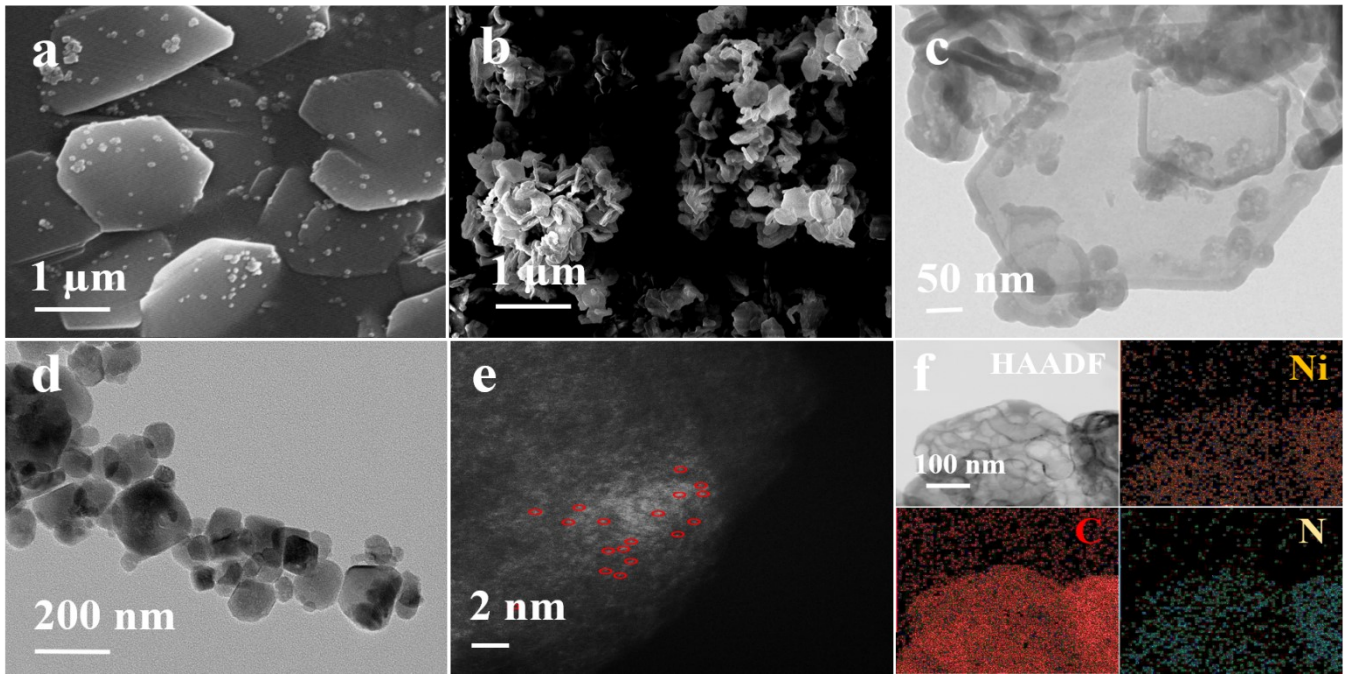

Fig. S4. (a) SEM of $Ni(OH)_2$; (b) SEM of Ni-N-C SAC; (c, d) TEM of Ni-N-C SAC; (e) Aberration corrected HAADF-STEM image of Ni-N-C SAC; (f) HAADF-STEM image and corresponding EDX mapping of Ni-N-C SAC.

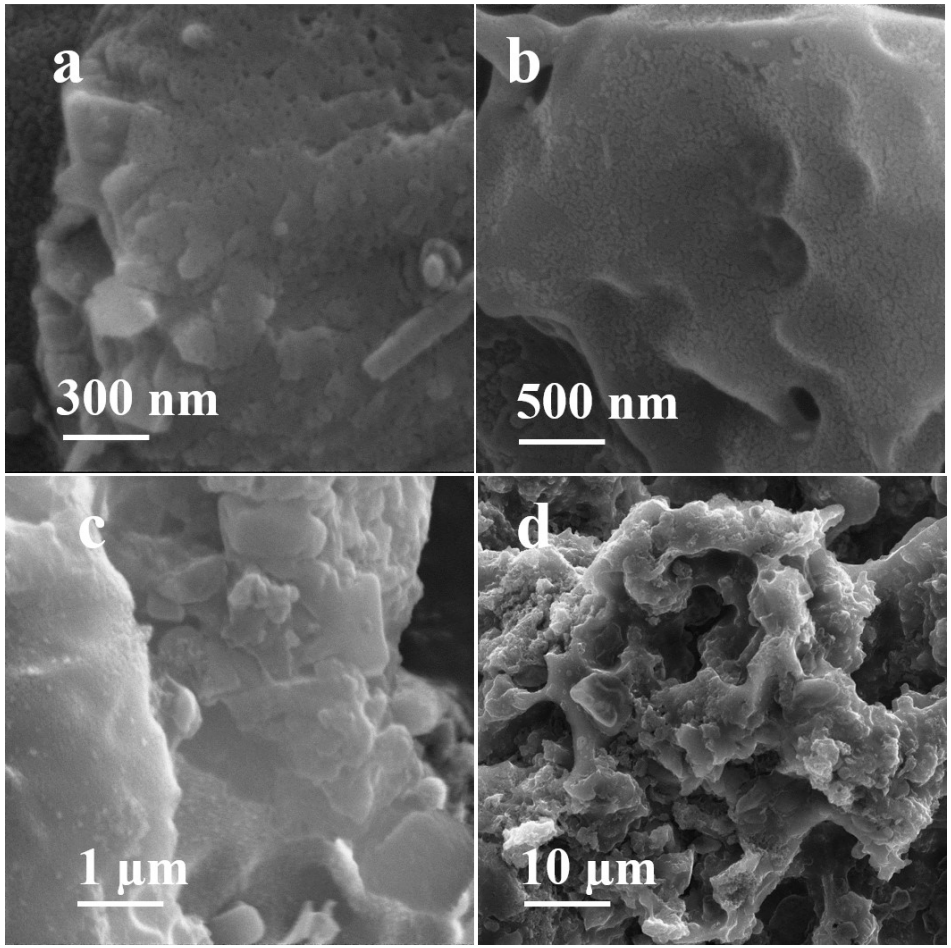

Fig. S5. SEM of NC sample.

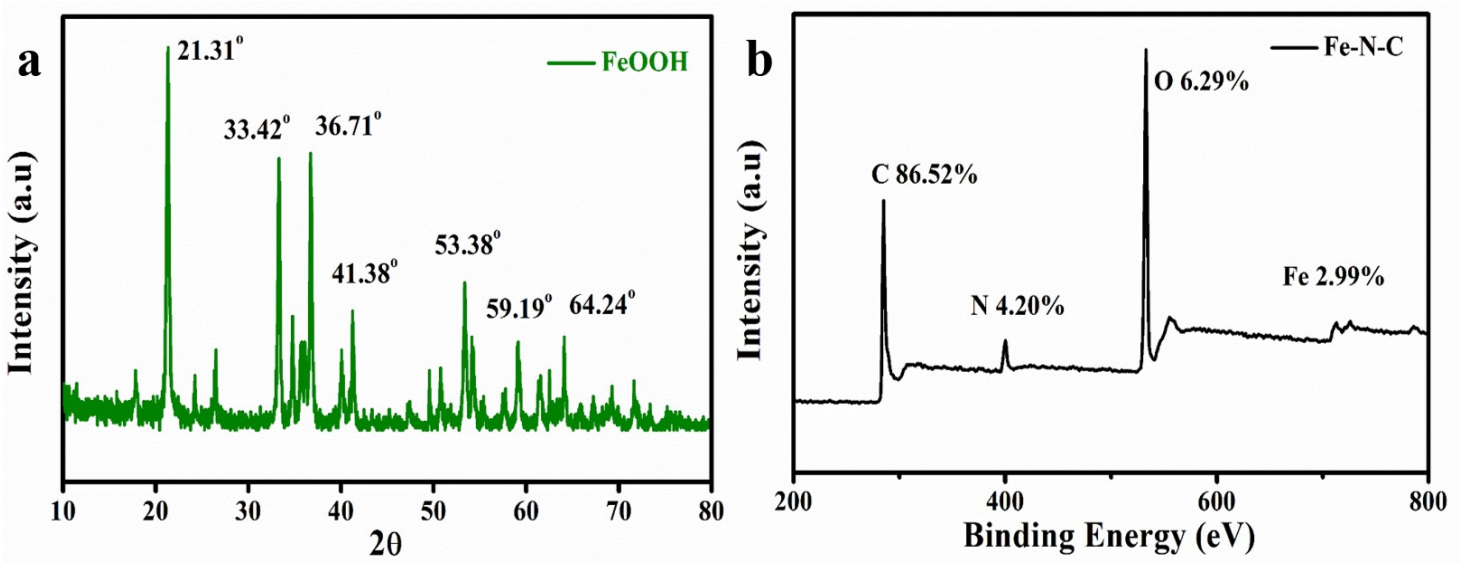

Fig. S6. (a) XRD of FeOOH; (b) XPS survey of Fe-N-C SAC.

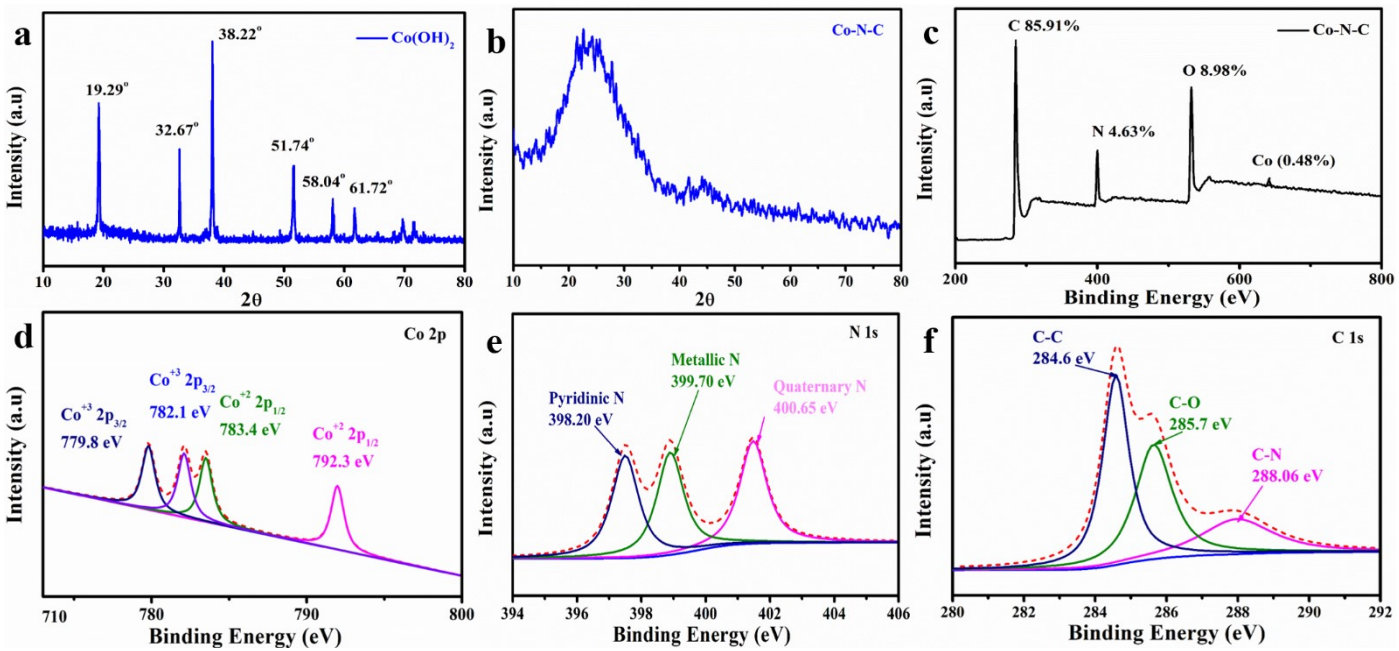

Fig. S7. XRD pattern of (a) $Co(OH)_2$; (b) Co-N-C SAC; (c) XPS survey of Co-N-C SAC; (d-f) Co 2p, N 1s, and C 1s of Co-N-C SAC.

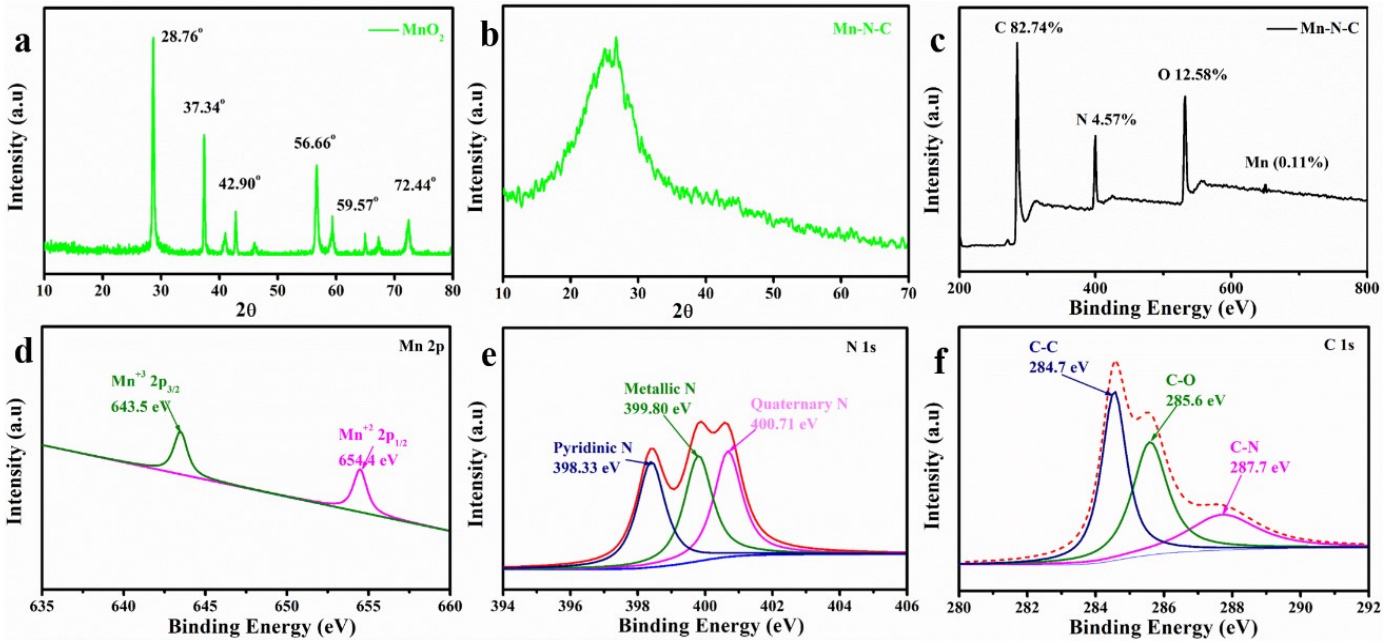

Fig. S8. XRD pattern of (a) MnO_2; (b) Mn-N-C SAC; (c) XPS survey of Mn-N-C SAC; (d-f) Mn 2p, N 1s, and C 1s of Mn-N-C SAC.

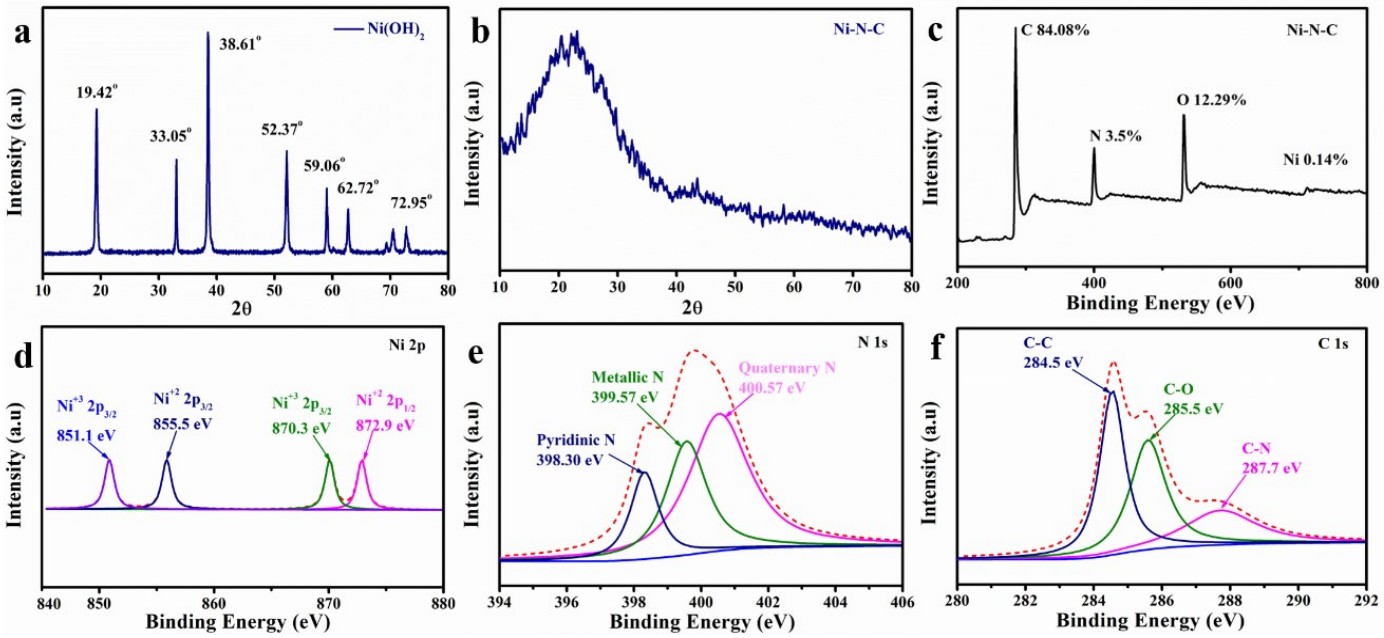

Fig. S9. XRD pattern of (a) $Ni(OH)_2$; (b) Ni-N-C SAC; (c) XPS survey of Ni-N-C SAC; (d-f) Ni 2p, N 1s, and C 1s of Ni-N-C SAC.

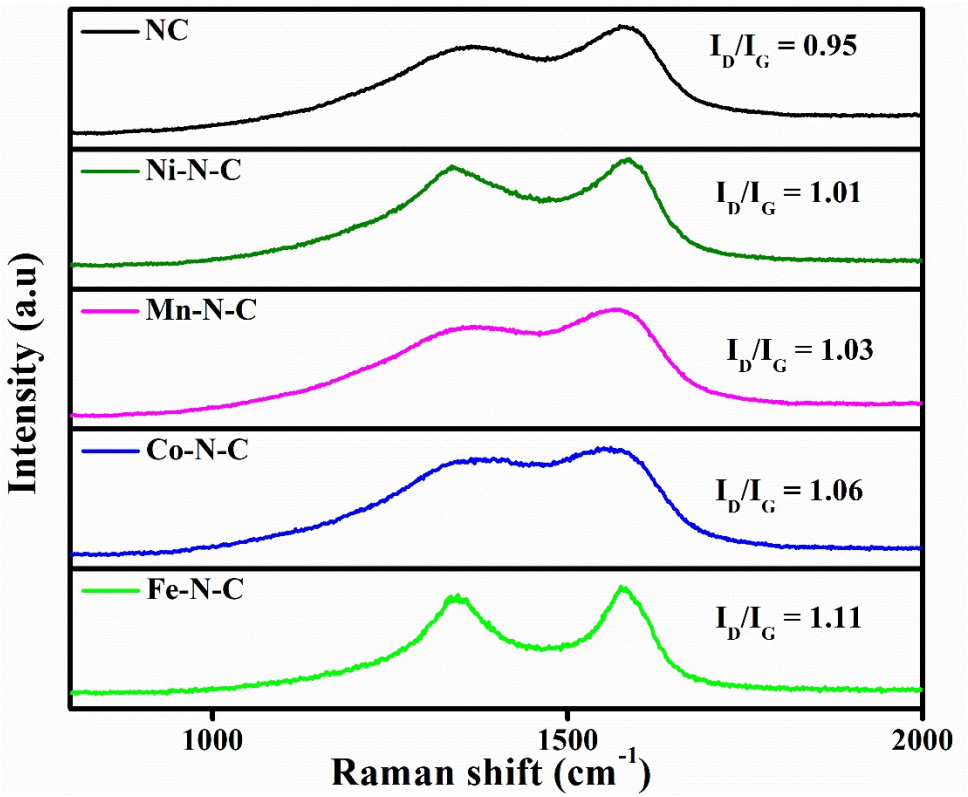

Fig. S10. Raman analysis results for Fe-N-C, Co-N-C, Mn-N-C, Ni-N-C, and NC.

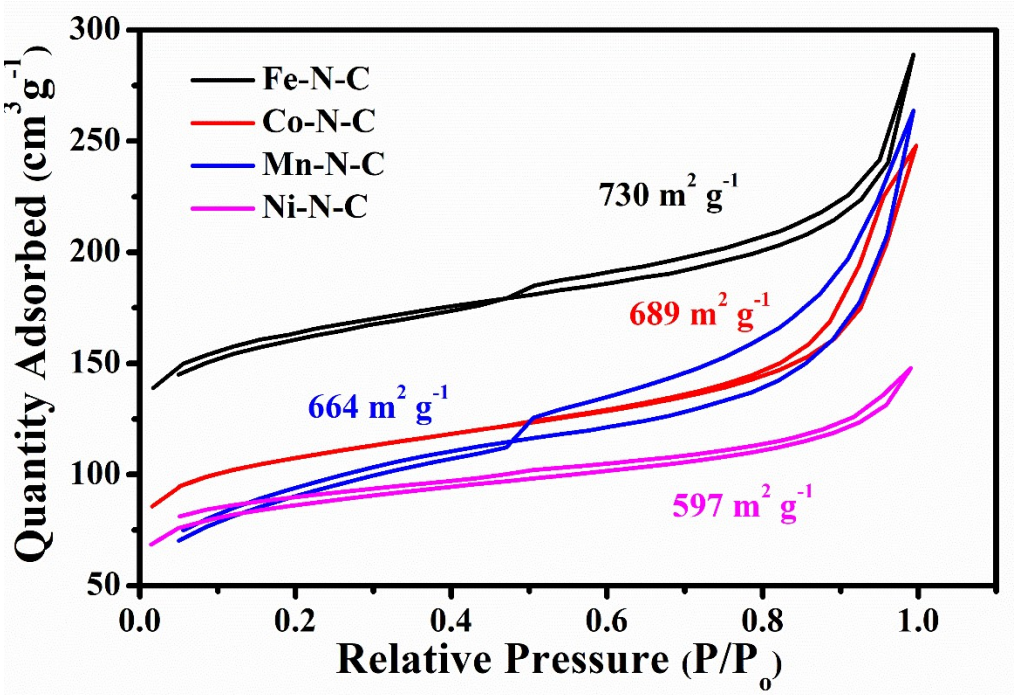

Fig. S11. N_2 adsorption desorption isotherms for Fe-N-C SAC, Co-N-C SAC, Mn-N-C SAC, and Ni-N-C SAC.

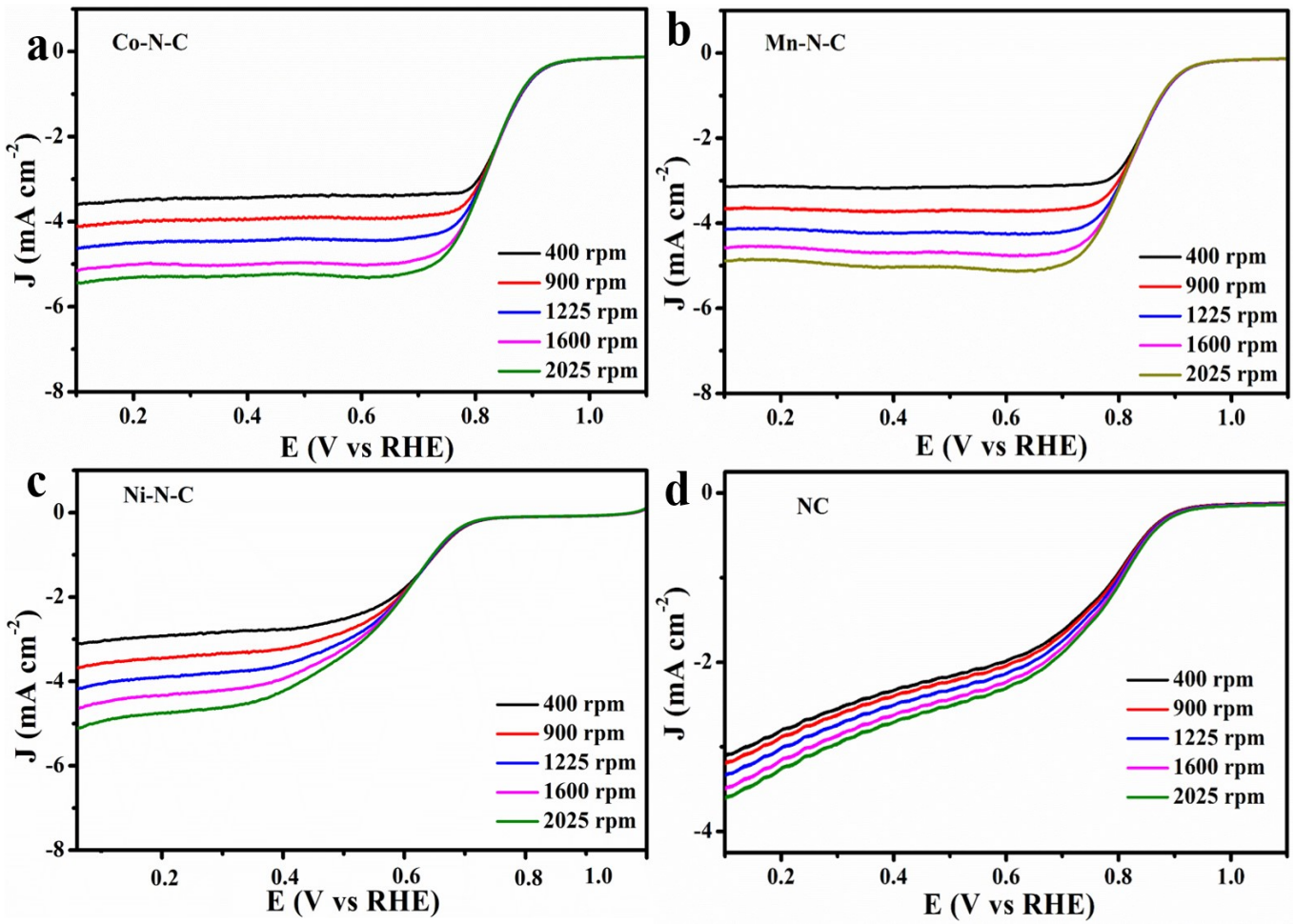

Fig. S12. LSV curves at different rpm in O_2 saturated 0.1 M KOH solution for (a) Co-N-C SAC; (b) Mn-N-C SAC; (c) Ni-N-C SAC; (d) NC.

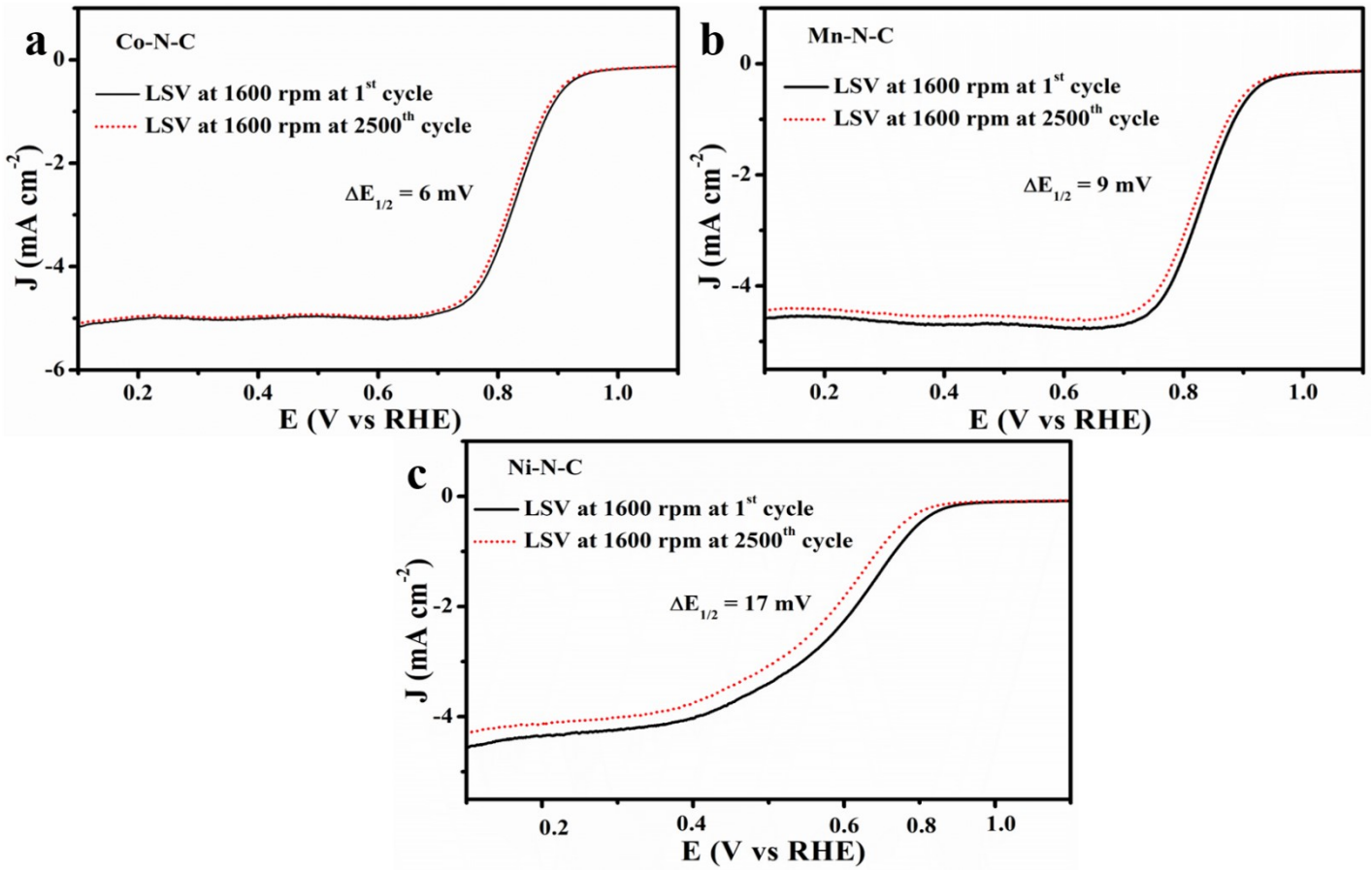

Fig. S13. LSV curves at 1600 rpm at 1st cycle and at 2500th cycle in O_2 saturated 0.1 M KOH solution for (a) Co-N-C SAC; (b) Mn-N-C SAC; (c) Ni-N-C SAC.

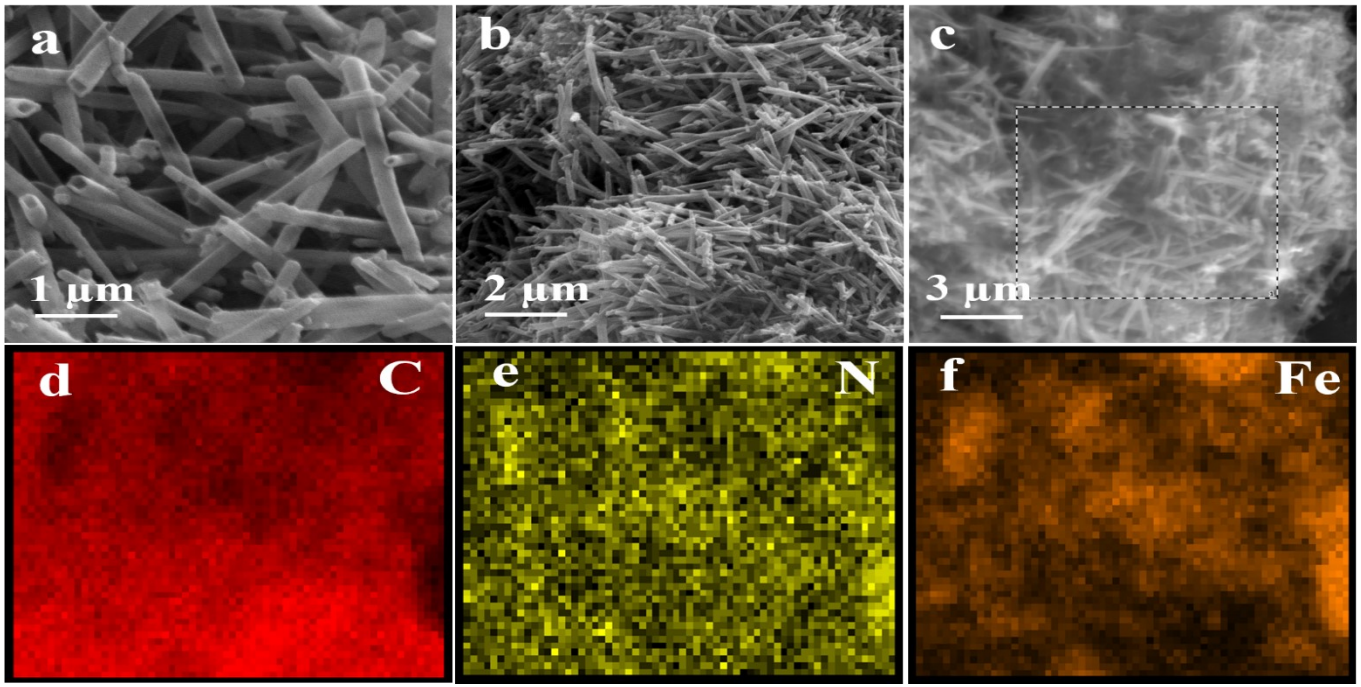

Fig. S14. (a, b) SEM for Fe-N-C after stability test of 2500th cycle, (c-f) corresponding EDS mapping.

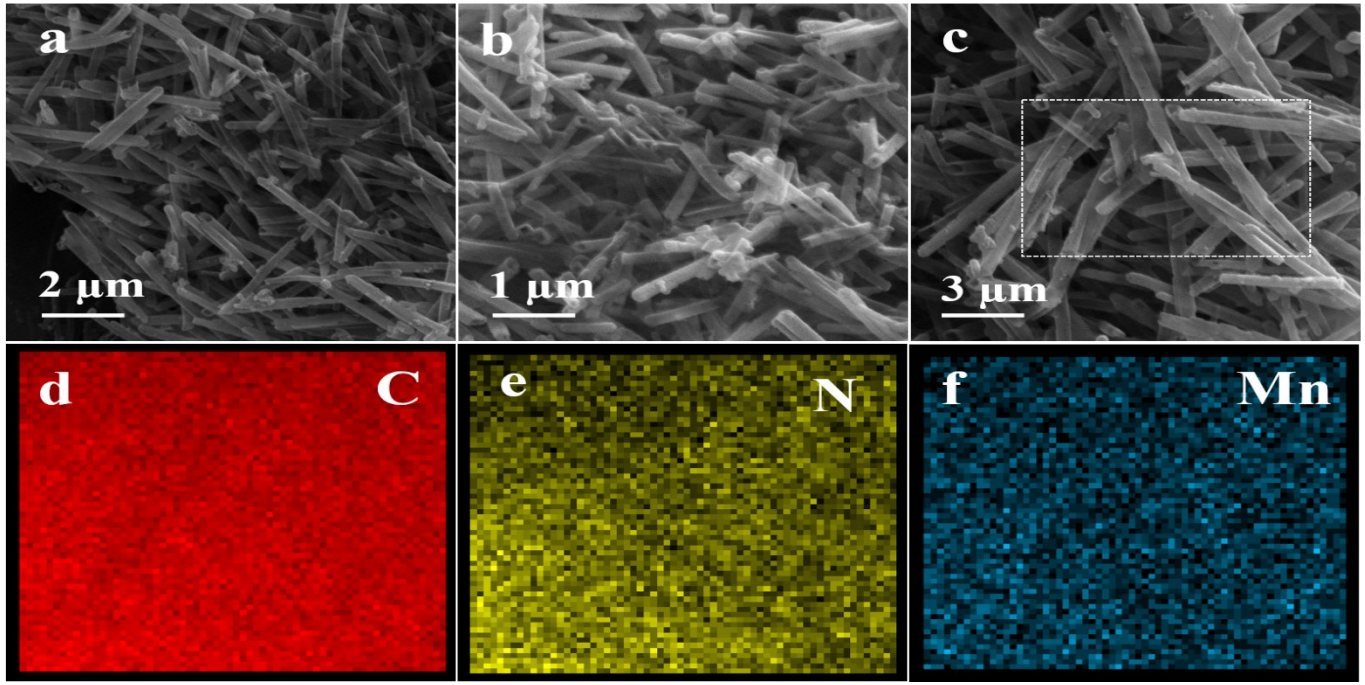

Fig. S15. (a, b) SEM for Mn-N-C after stability test of 2500th cycle, (c-f) corresponding EDS mapping.

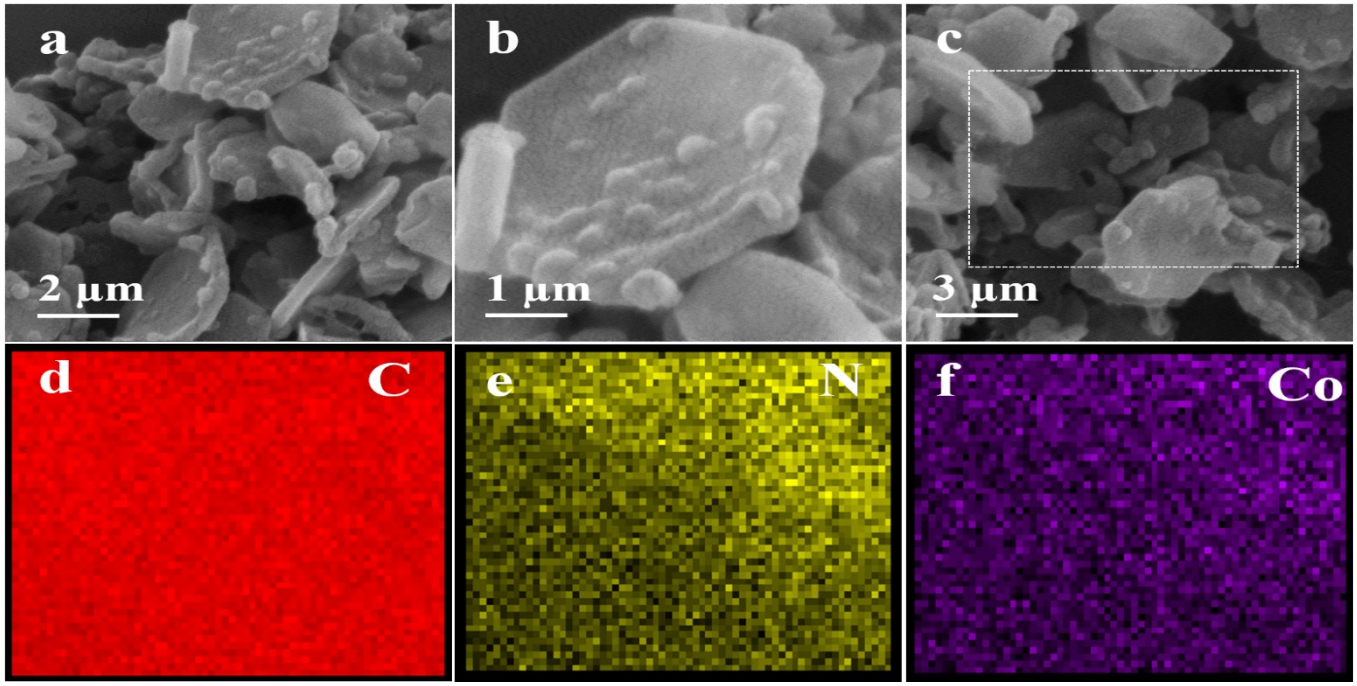

Fig. S16. (a, b) SEM for Co-N-C after stability test of 2500th cycle, (c-f) corresponding EDS mapping.

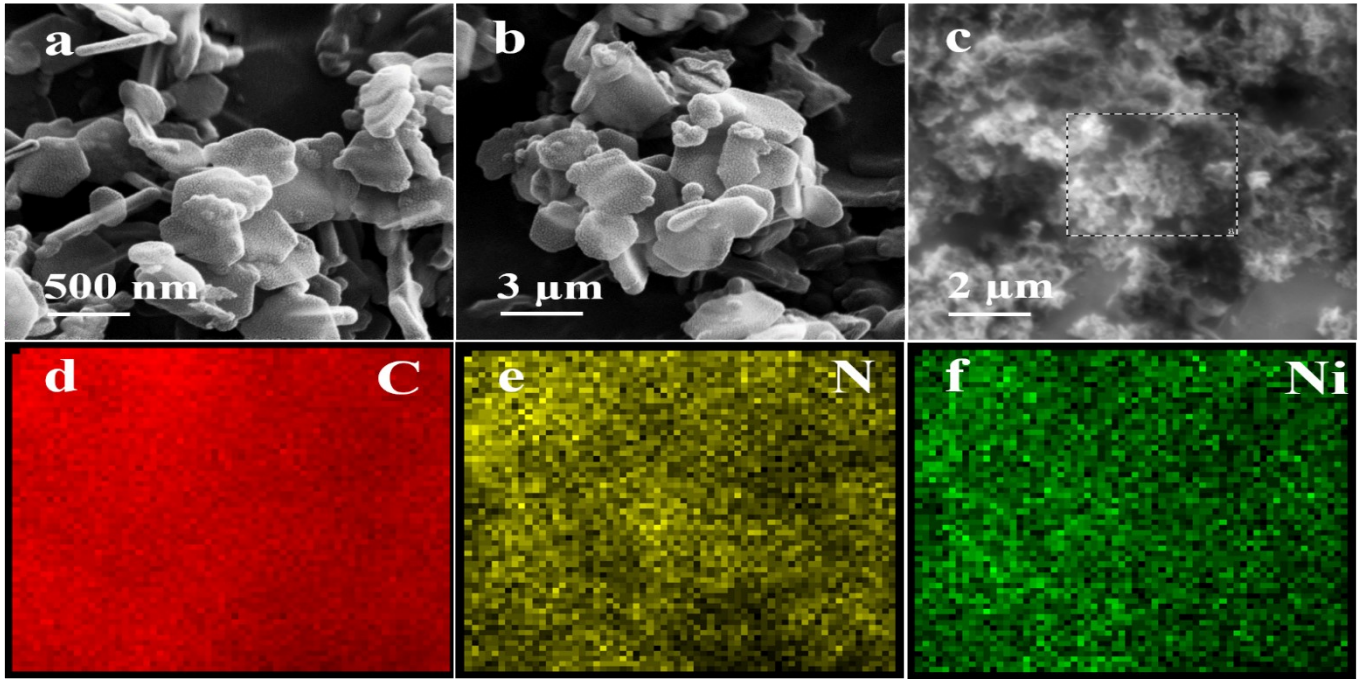

Fig. S17. (a, b) SEM for Ni-N-C after stability test of 2500th cycle, (c-f) corresponding EDS mapping.

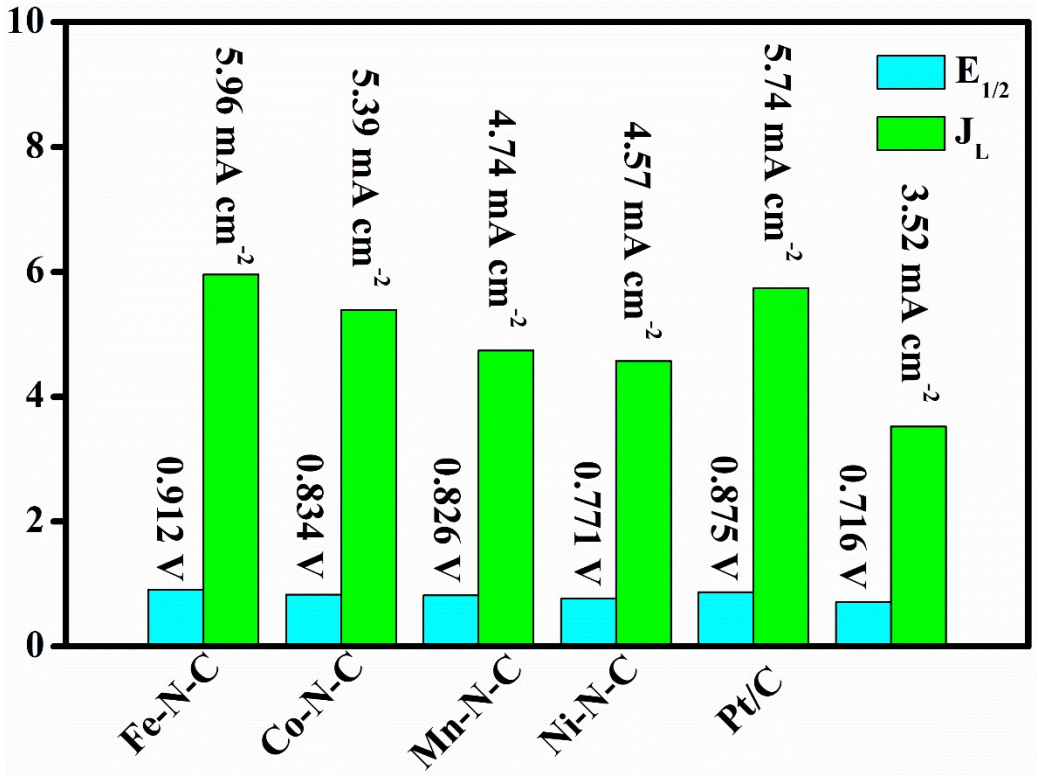

Fig. S18. Comparative ORR catalytic performance in O_2 saturated 0.1 M KOH solution for the Fe-N-C SAC, Co-N-C SAC, Mn-N-C SAC, Ni-N-C SAC, 20% Pt/C, and NC.

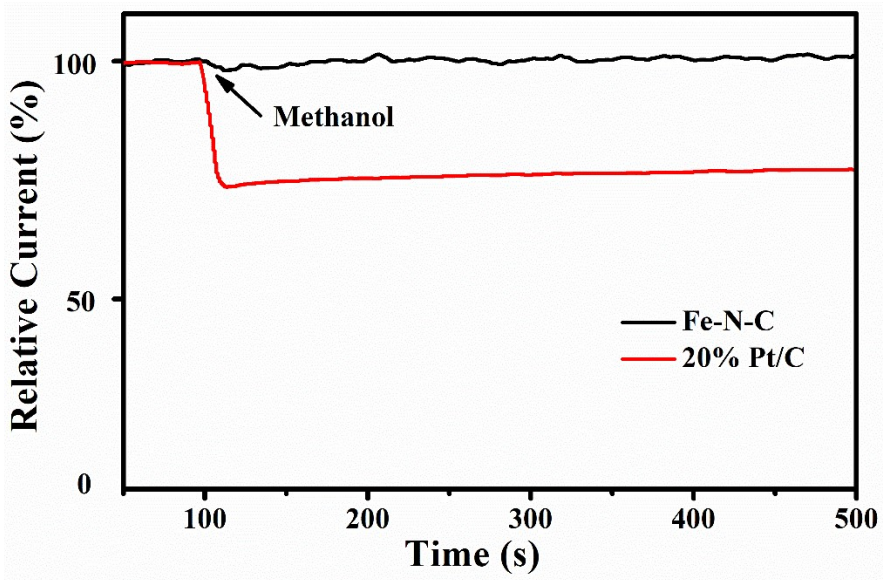

Fig. S19. Methanol tolerance test for Fe-N-C SAC and 20% Pt/C.

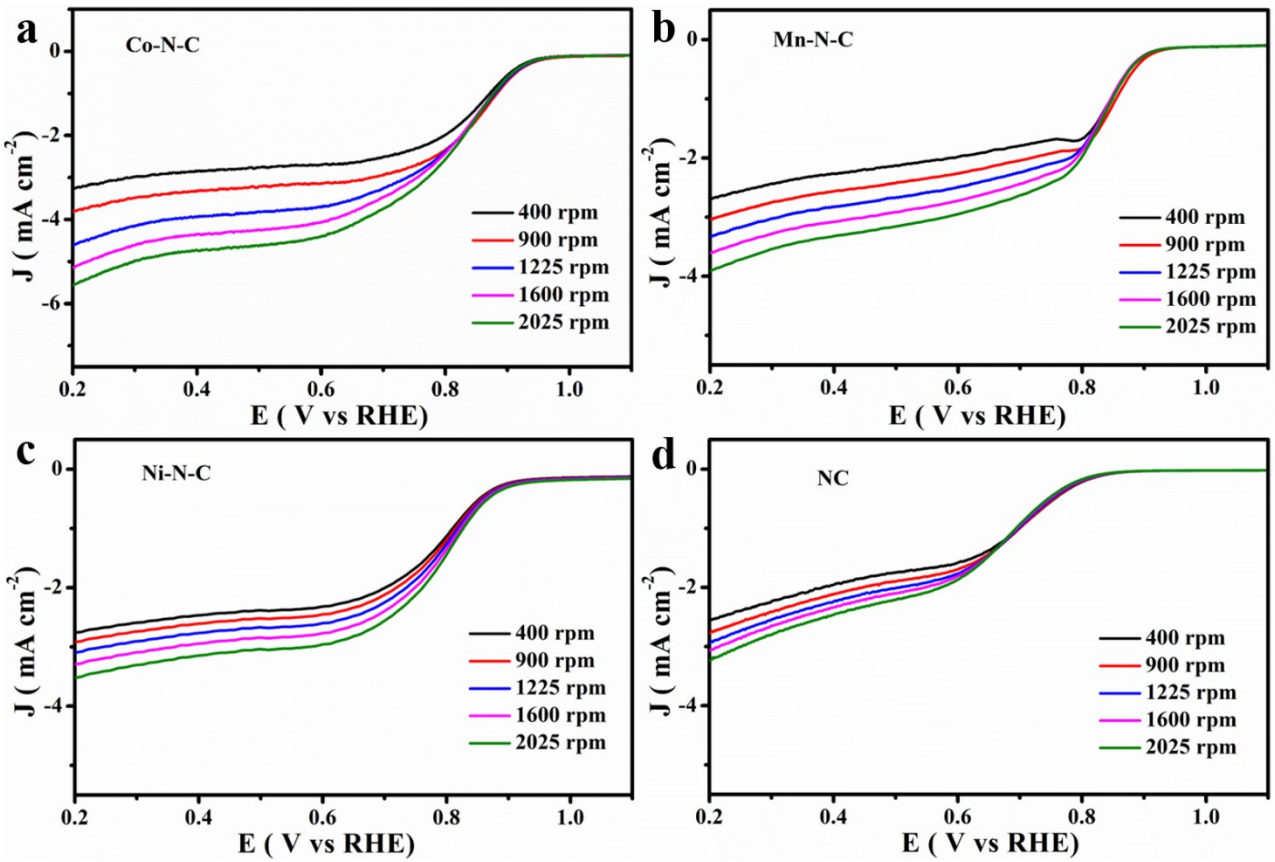

Fig. S20. LSV curves at different rpm in O_2 saturated 0.1 M $HClO_4$ solution for (a) Co-N-C SAC; (b) Mn-N-C SAC; (c) Ni-N-C SAC; (d) NC.

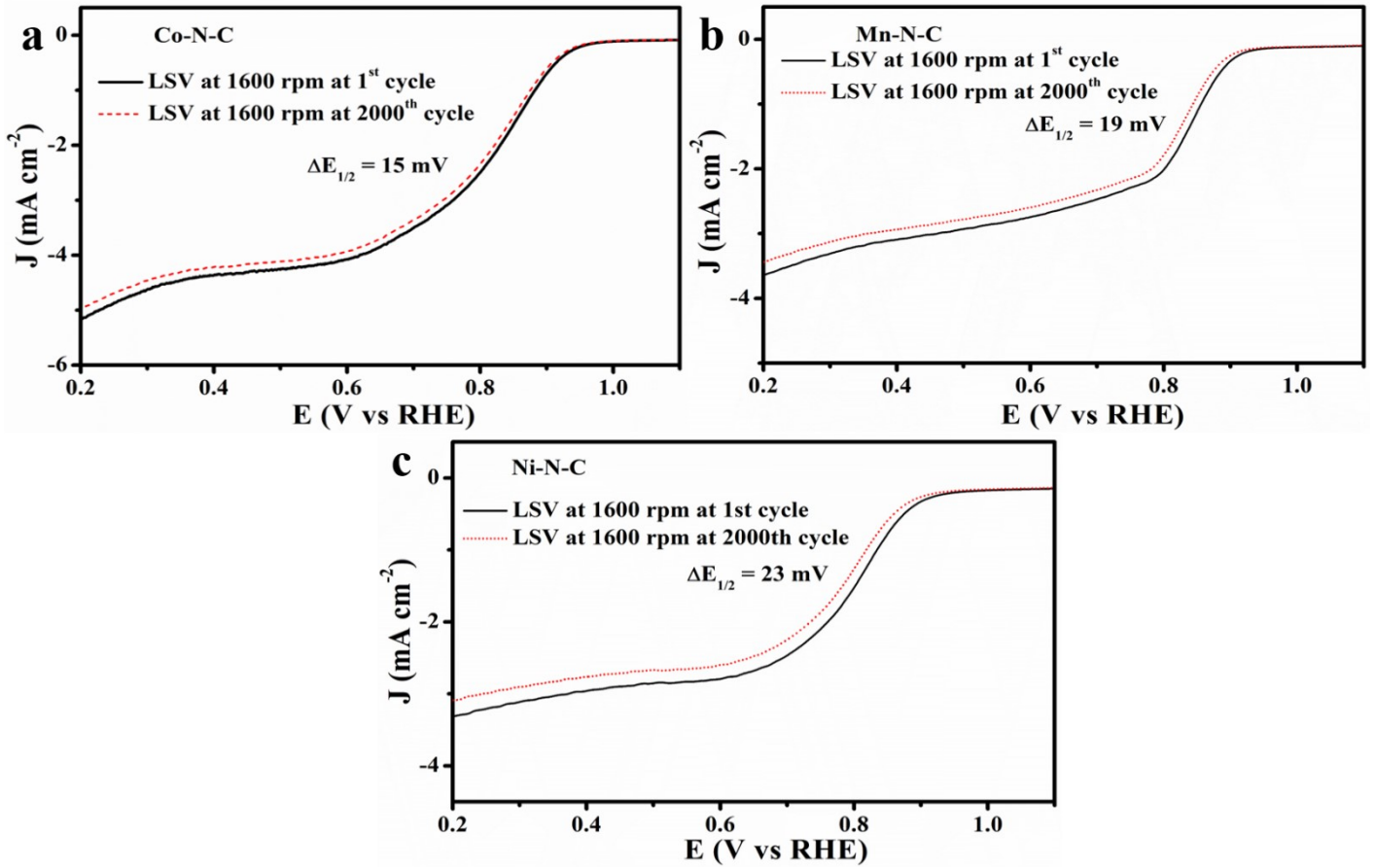

Fig. S21. LSV curves at 1600 rpm at 1st cycle and after 2000th cycle in O_2 saturated 0.1 M $HClO_4$ solution for (a) Co-N-C SAC; (b) Mn-N-C SAC; (c) Ni-N-C SAC.

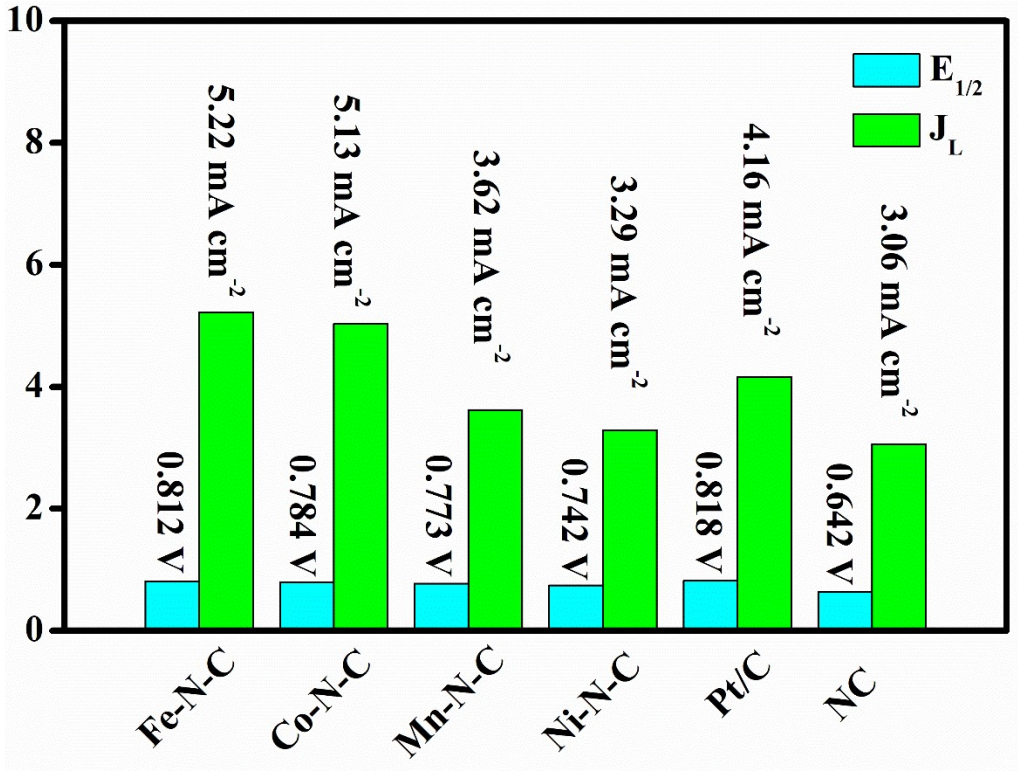

Fig. S22. Comparative ORR catalytic performance in O_2 saturated 0.1 M $HClO_4$ solution for Fe-N-C SAC, Co-N-C SAC, Mn-N-C SAC, Ni-N-C SAC, 20% Pt/C, and NC.

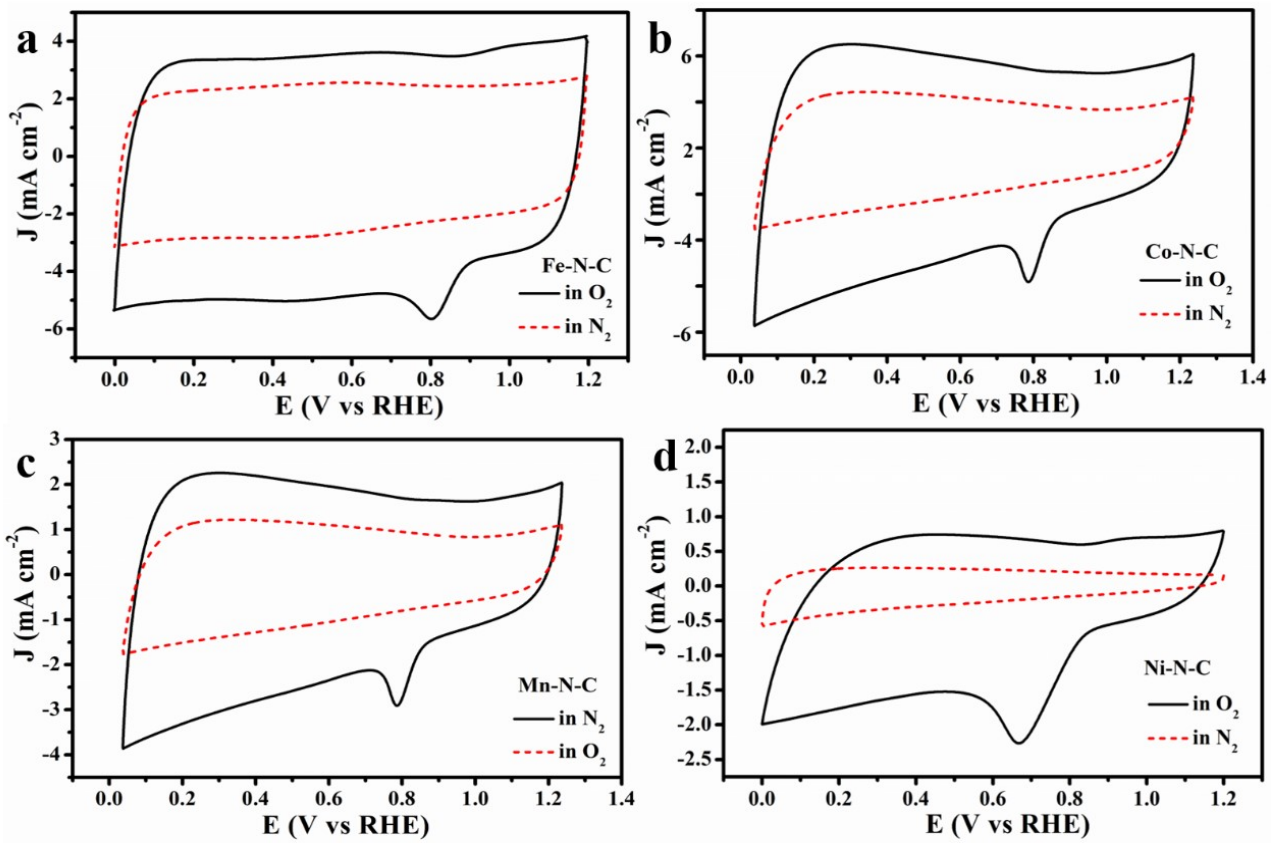

Fig. S23. CV curves in 0.1 M KOH for (a) Fe-N-C SAC; (b) Co-N-C SAC; (c) Mn-N-C SAC; (d) Ni-N-C SAC.

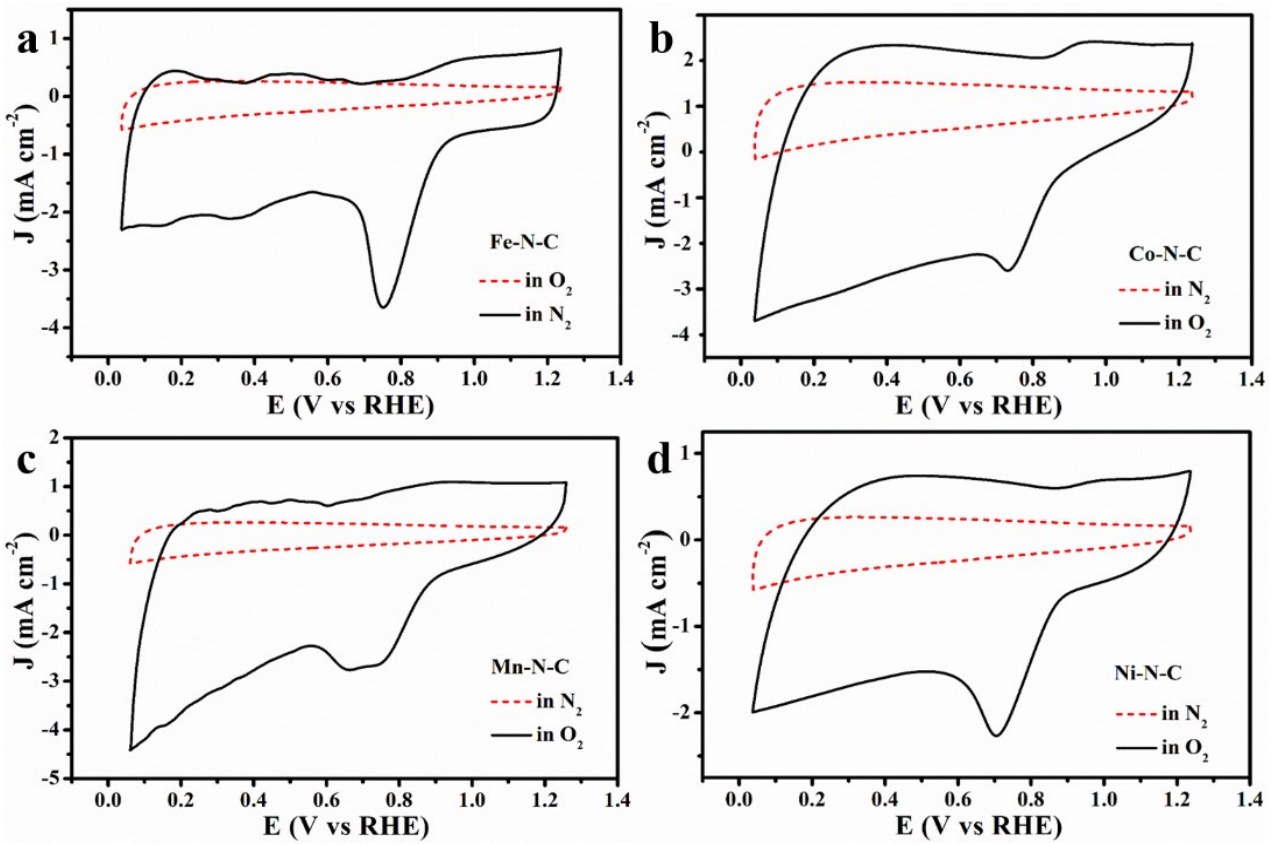

Fig. S24. CV curves in 0.1 M $HClO_4$ for (a) Fe-N-C SAC; (b) Co-N-C SAC; (c) Mn-N-C SAC; (d) Ni-N-C SAC.

Table S1: Fe atomic percentage from ICP-OES

Catalyst	**Metal content (wt. %)**
Fe-N-C	2.83
Co-N-C	0.97
Mn-N-C	0.86
Ni-N-C	0.79

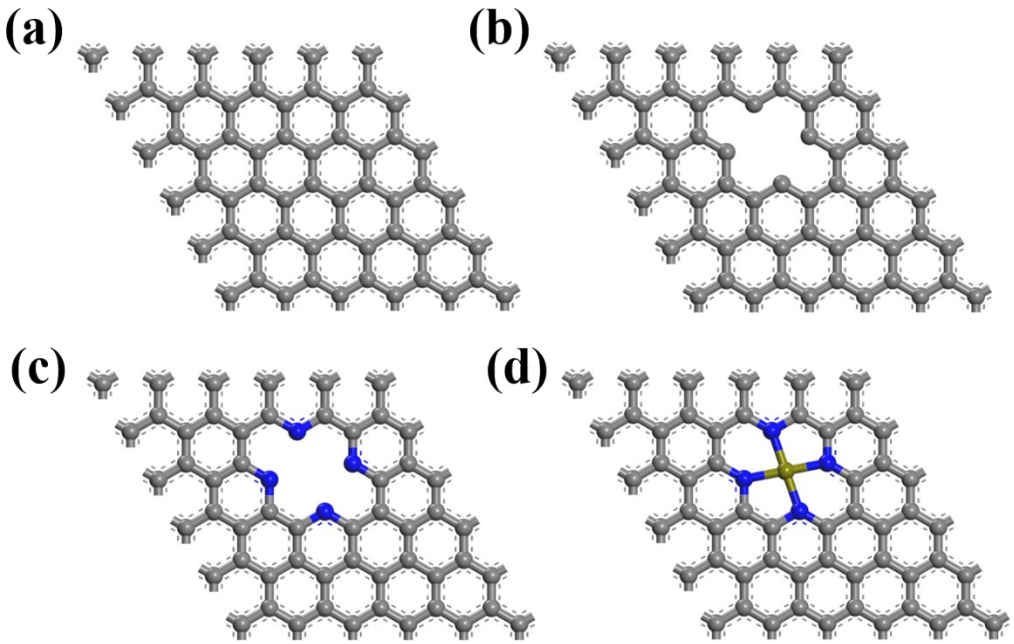

Fig. S25. (a) Graphene, (b) graphene quadruple vacancy (QV), (c) graphene quadruple vacancy (QV) with N atoms, (d) M-N-C. Grey: C, blue: N, and green: M (M = Fe, Co, Mn, and Ni) atoms, respectively.

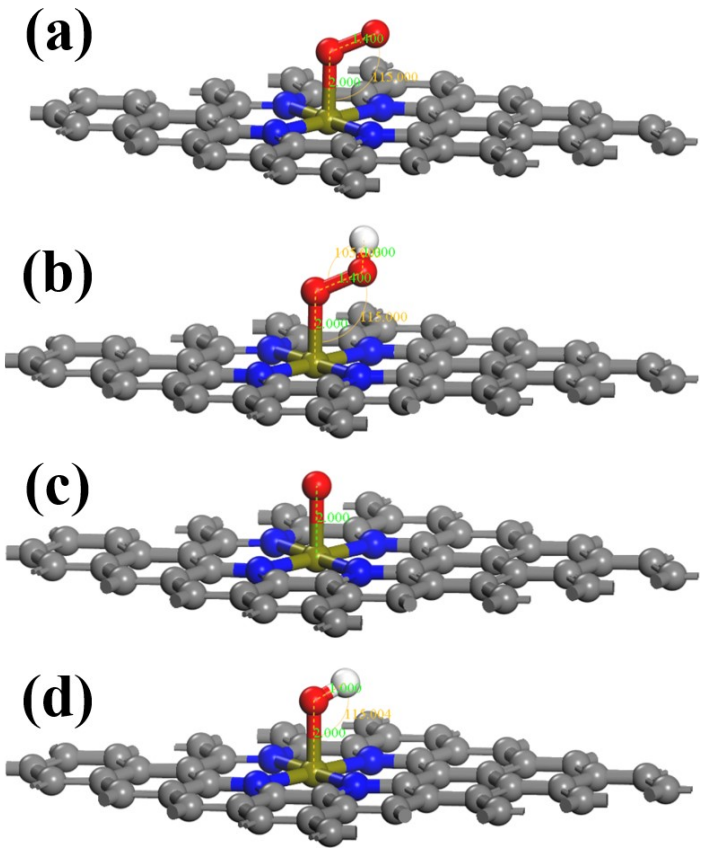

Fig. S26. Intermediates (a) O_2, (b) -OOH, (c) O*, and (d) OH* on M-N-C.

Table S2: Comparative literature for M-N-C SAC catalyst

Catalyst	**Loading amount of the catalyst (mg cm^{-2})**	**$E_{1/2}$ in acid (V)**	**$E_{1/2}$ in base (V)**	**ZAB Performance (mW cm^{-2})**	**Reference**
Co@NC-MOF	0.6	0.72	0.88	-	[1]
Co-N-C	0.8	-	0.85	227	[2]
Co-N-C			0.82	135	[3]
Fe–N–C	0.6	0.80	0.88	-	[4]
Fe–N–C	0.65	-	0.82	-	[5]
Fe–N–C-NH_3	0.4	0.65	0.85	-	[6]
Fe-N-C	0.4	-	0.87	185	[7]
Mn-N-C	0.6	-	0.81	-	[8]
Fe-N-C	0.6	-	0.83	71.6	[9]
Fe-N-C	0.5	-	0.89	-	[10]
Mn-N-C	0.8	0.74	-		[11]
Fe-N-C	0.4	0.80	0.91	185	**This work**

Co-N-C	0.78	0.83
Mn-N-C	0.77	0.82
Ni-N-C	0.72	0.76

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