

Electronic Supplementary Information

A polypyrrole derived nitrogen doped porous carbon support for atomically dispersed Mn electrocatalyst for oxygen reduction reaction

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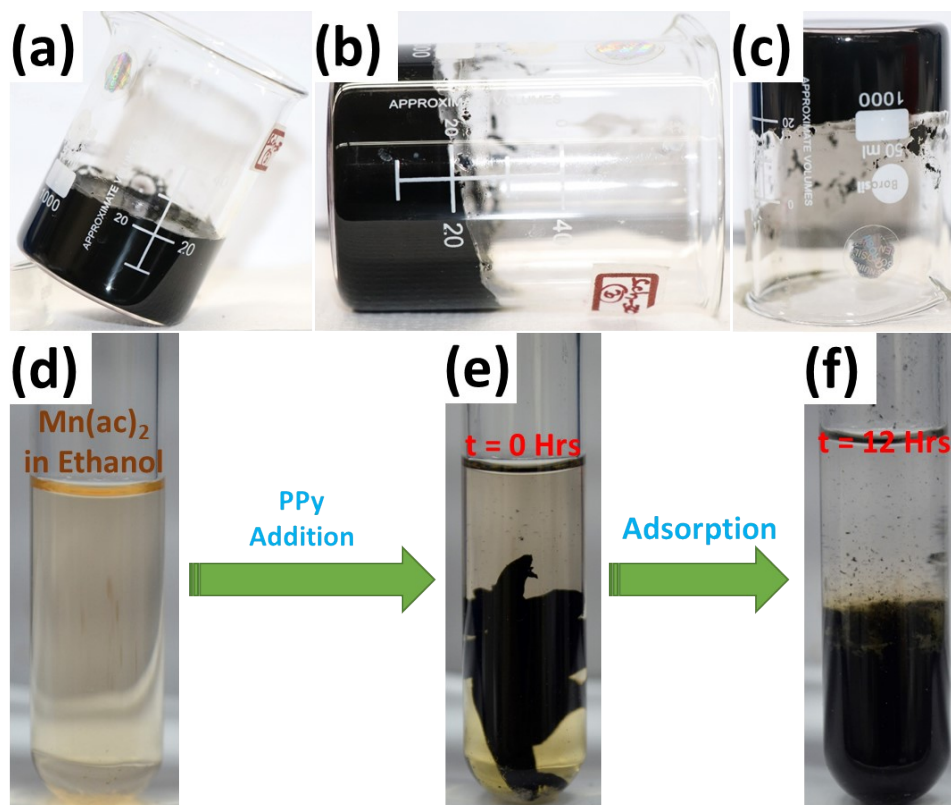


Fig. S1 Photographs of PPy hydrogel (a)-(c) and Mn(ac)₂ loaded PPy at different time intervals (d)-(g).

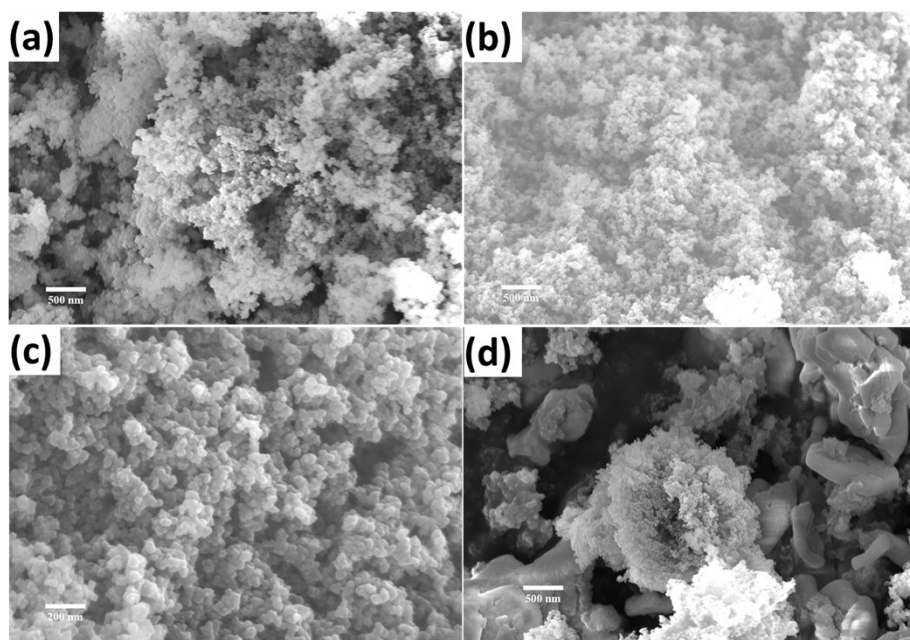


Fig. S2 FESEM images of (a) 0Mn@PPy (b, c) 0.01Mn@PPy (d) 0.1Mn@PPy.

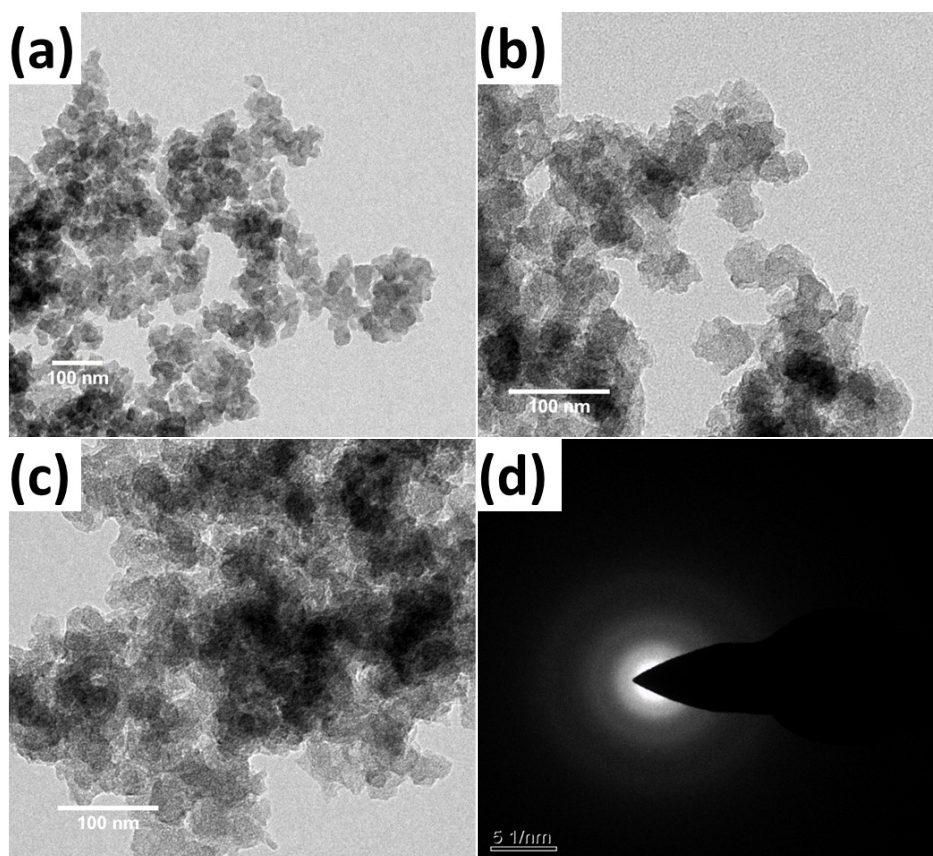


Fig. S3 Representative TEM images of (a) 0Mn-N-C, (b) 0.01Mn-N-C, (c) 0.1Mn-N-C and (d) SAED pattern of 0.01Mn-N-C.

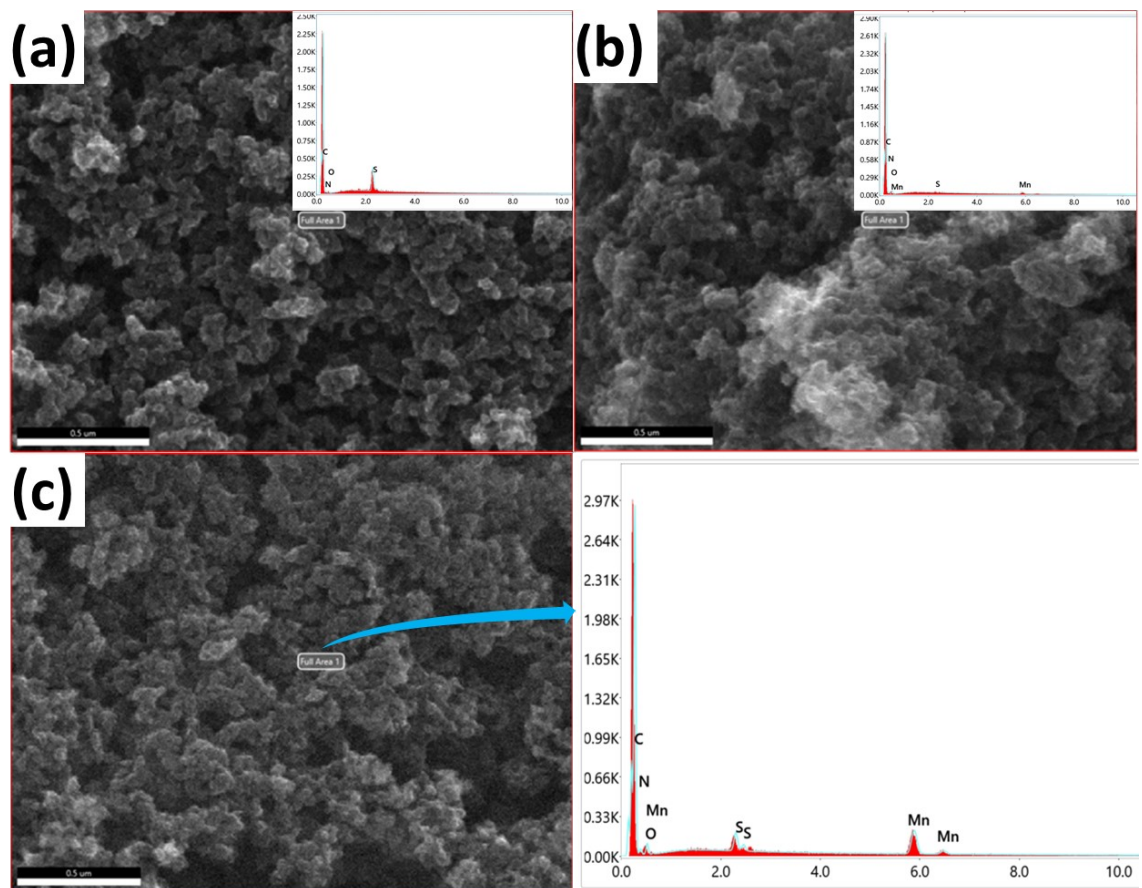


Fig. S4 SEM image with corresponding EDX pattern of (a) 0Mn-N-C, (b) 0.1Mn-N-C and (c) 0.01Mn-N-C.

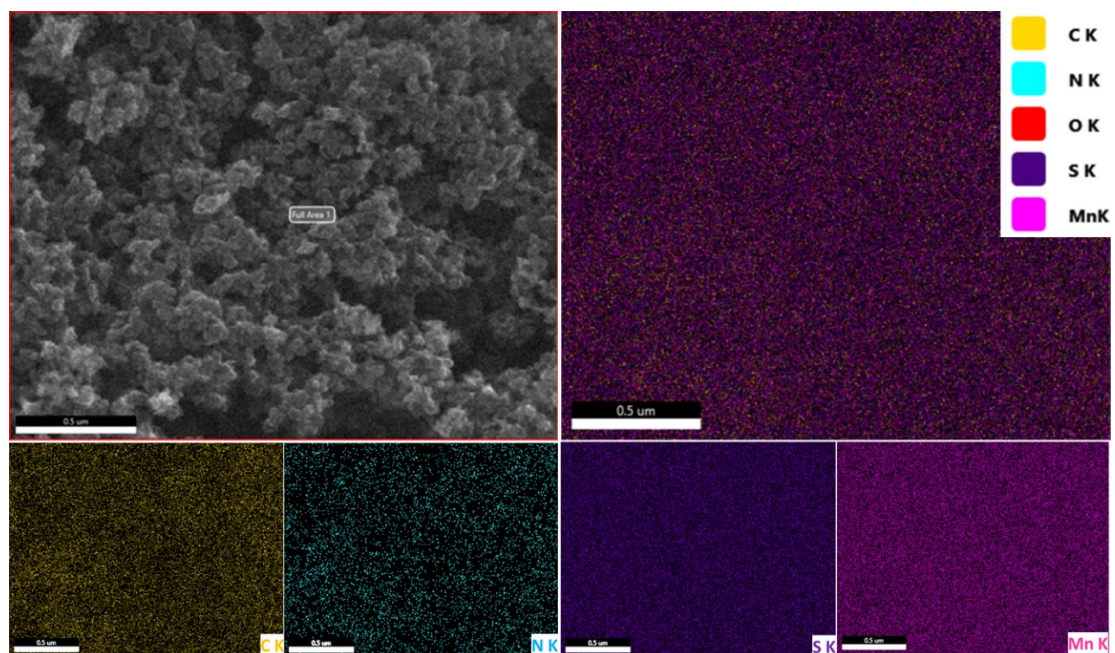


Fig. S5 SEM image with EDX elemental mapping of 0.01Mn-N-C.

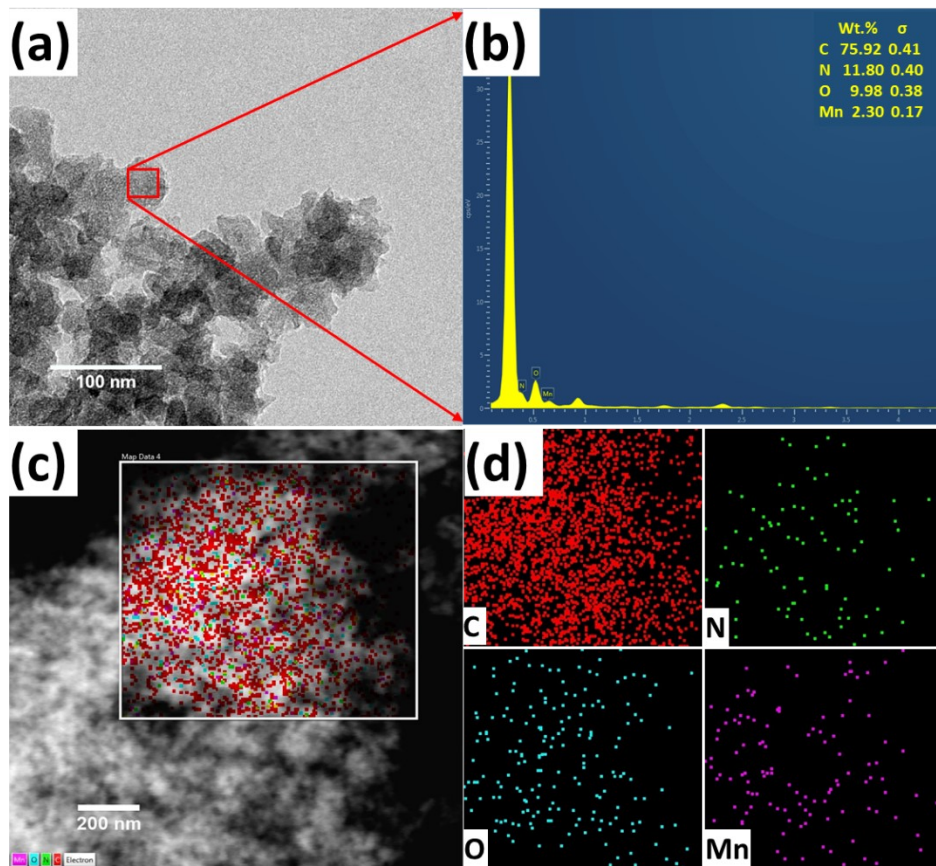


Fig. S6 (a) STEM image, (b) EDS pattern and (c, d) EDX elemental mapping of 0.01Mn-N-C.

Table S1. BET surface area and pore size of the catalysts.

Catalyst	SA_{BET} (m ² /g)	SA_{Micro} (m ² /g)	V_{Micro} (cc/g)	V_{Meso} (cc/g)	V_{Total} (cc/g)
0Mn-N-C	411.485	168.369	0.073	0.390	1.487
0.01Mn-N-C	492.621	49.466	0.024	0.432	1.590
0.1Mn-N-C	209.104	11.023	0.006	0.203	0.2639

Table S2. Elemental composition of catalysts as obtained from XPS and ICP-OES.

Catalyst	At. % Composition (XPS)					Wt.% (ICP-OES)
	C	N	O	S	Mn	Mn
0Mn-N-C	86.5	9.1	3.5	0.9	0.0	0.00
0.01Mn-N-C	80.2	8.8	7.6	1.6	1.8	2.66
0.1Mn-N-C	86.3	6.2	6.1	0.3	0.8	1.90

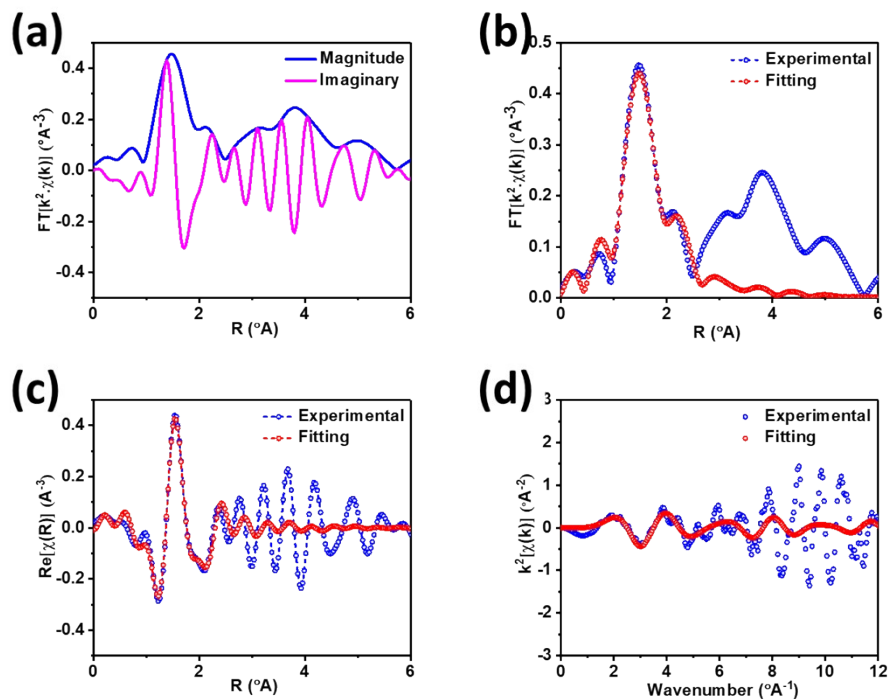


Fig. S7 (a) The magnitude and imaginary part of the FT-EXAFS of 0.01Mn-N-C. The experimental and fitting curves of FT-EXAFS of 0.01Mn-N-C in (b, c) R-space and (d) k-space.

Table S3. Fitting parameters of Mn K-edge EXAFS for 0.01Mn-N-C.

Path	N	R (°Å)	σ^2	ΔE_0 (eV)	R-factor
Mn-N	4	2.067±0.025	0.0009±0.0029	1.286±1.848	0.091

N: Coordination number; **R:** the distance between absorber and backscatter atoms (equals to the bond length of Mn-N); **σ^2 :** the Debye-Waller factor value; **ΔE_0 :** the inner potential correction to account for the difference in the inner potential between the sample and the reference compound.

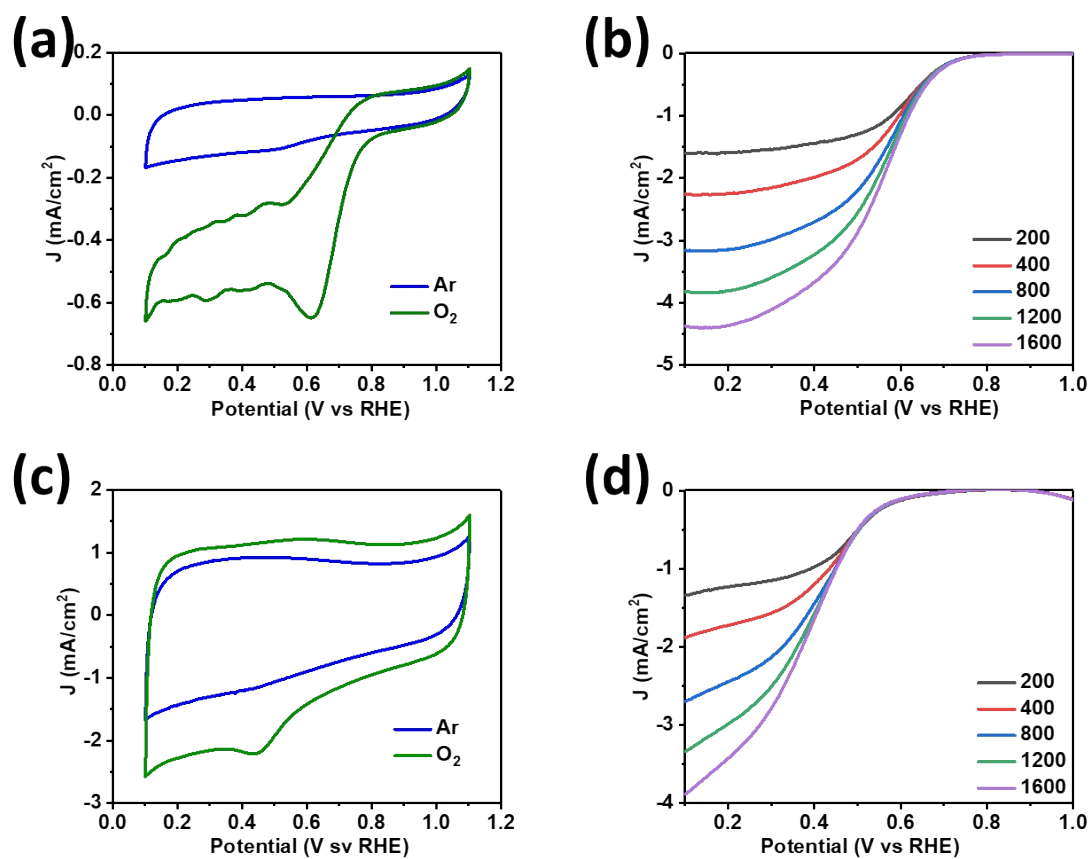


Fig. S8 (a) CV, (b) LSV of 0.01Mn-N-C and (c) CV, (d) LSV of 0Mn-N-C in 0.5M H₂SO₄.

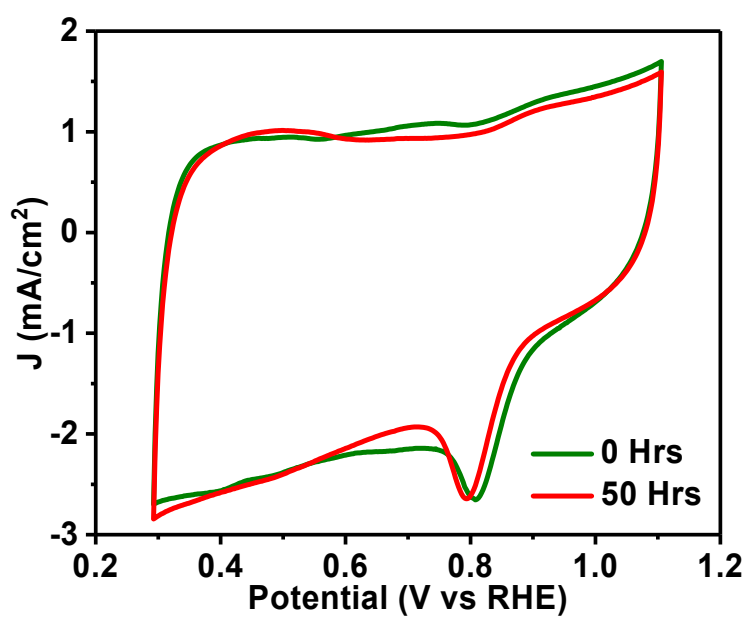


Fig. S9 CV of 0.01Mn-N-C after chronoamperometric test at 0.7V vs RHE at 1600 RPM in O₂ saturated 0.1M KOH.

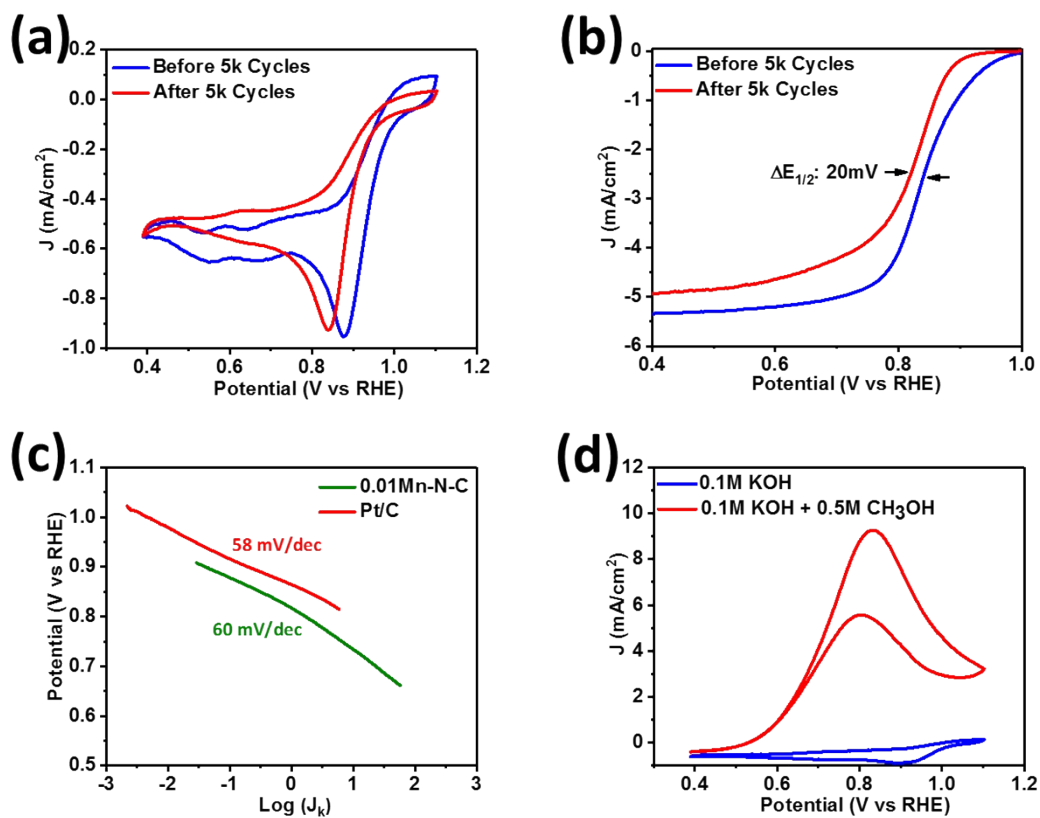


Fig. S10 (a) CV and (b) LSV of Pt/C before and after accelerated durability test (ADT). (c) Tafel slopes of 0.01Mn-N-C and Pt/C after ADT. (d) CV of Pt/C in O₂ saturated 0.1M KOH and 0.1M KOH+0.5M CH₃OH in methanol tolerance test.

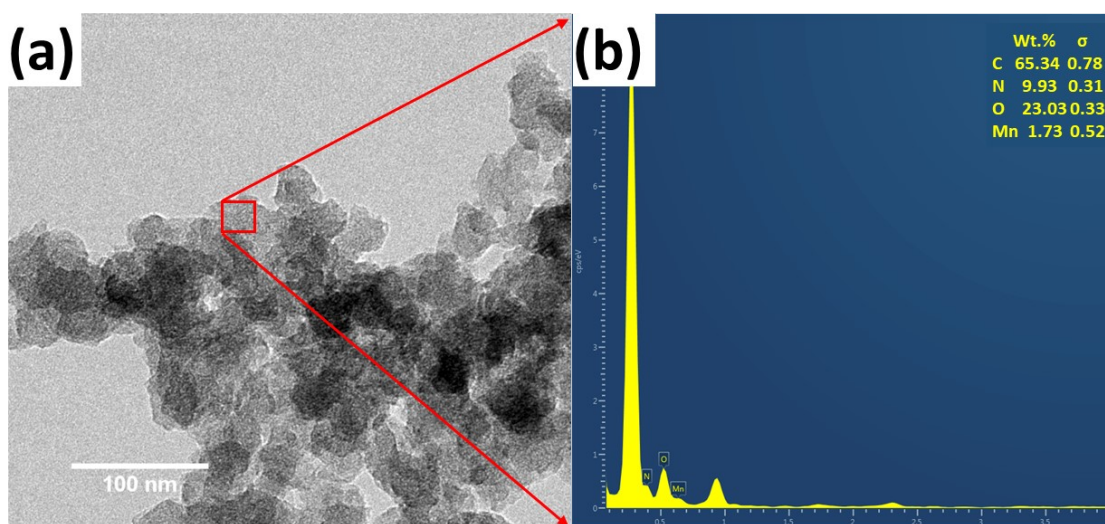


Fig. S11 (a) STEM image and (b) corresponding EDX pattern of 0.01Mn-N-C after ADT.

Table S3. Review of ORR activity of Mn single-atom catalysts in 0.1M KOH reported in recent literature.

Catalyst	Mn Content	Loading ($\mu\text{g}/\text{cm}^2$)	E_{on} (V vs RHE)	$E_{1/2}$ (V vs RHE)	Ref.
0.01Mn-N-C	2.66 wt%	400	0.91	0.82	This work
MnNC	7.88 wt%	500	0.97	0.86	[1]
Mn-N-C-OAc-10-Second	0.36 at%	800	-	0.94	[2]
Mn-NAHPC-900	0.76 wt%	263	0.96	0.86	[3]
Mn-SA	1.8 wt%	200	0.99	0.87	[4]
Mn-N-C900	0.27 at%	600	0.98	0.88	[5]
MnSAC	1.85 wt%	102	1.04	0.915	[6]
MnN ₄ @rGO	-	250	0.91	0.86	[7]
Mn@NG	0.5 wt%	300	0.95	0.82	[8]
MnNPC-900	0.39 wt%	400	0.97	0.84	[9]
f-MnNC/CNT-170	0.67 at%	260	0.91	0.83	[10]

References:

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