Ultrathin atomic Mn-decorated formamide-converted N-doped carbon for efficient oxygen reduction reaction

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1. Experimental

1.1 Materials

Formamide (FA, purity>99%) was purchased from Xilong Chemical Co., Ltd. Manganese chloride ($MnCl_2$) was purchased from Tianjin Fuchen Chemical Research Factory. Carbon nanotube (CNT) was purchased from Nanjing XFNANO Material Technology Co., Ltd. Nitric acid (HNO_3, 65 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd. N, N-dimethylformamide (DMF, purity>99.5%) was purchased from Aladdin reagent Co., Ltd. The commercial Pt/C catalyst (20 wt.%, ~3 nm Pt nanoparticles on Vulcan XC-72 carbon support) was purchased from Shanghai MackLin biochemical technology co. LTD. The Nafion and ethanol solution (~5 wt.%) were purchased from Sigma-Aldrich Co., LTD. Deionized water with a resistivity >18 MΩ was used to prepare all aqueous solutions. All the reagents were of analytical grade and were used without further purification.

1.2 Characterization

The morphologies of as-prepared samples were characterized by transmission electron microscopy (Hitachi-7700, 100 kV) and high-resolution transmission electron microscope including (JEOL 2100, 200 kV). High-Angle Annular Dark Field-Scanning Transmission Electron Microscope (HAADF-STEM) was utilized to record the atomic state of the prepared catalysts. X-ray diffraction (XRD) patterns were collected on (UItima III, 3kw), recorded with 2θ ranging from 3° to 80°. Raman spectra were collected LabRAM Aramis Raman spectrometer (HORIBA Jobin Yvon, 500-3000 cm-1) with 532 nm line of Ar laser as excitation source. XPS measurements were carried out with Thermo Electron ESCALAB250 XPS Spectrometer.

XAFS spectra at the Mn K-edge was measured at the beamline 1W1B station of the Beijing Synchrotron Radiation Facility (BSRF), China. The Mn K-edge XAFS data of f-MnNC/CNT was recorded in a fluorescence mode. Mn foil and MnO_2 were used as references in a transmission mode. The acquired EXAFS data were processed with the

ATHENA module. The k^3-weighted EXAFS spectra in the k-space ranging from 2-10 $Å^{-1}$ were Fourier-transformed to real (R) space using a Hanning windows. The data fitting were completed with Artemis software.

1.3 Catalyst preparation

The preparation of f-MnNC/CNT was synthesized via solvothermal method. The pre-oxidation of carbon nanotubes was carried out in nitric acid for 120 minutes at 80 ℃. Then the mixed acid solution was allowed to cool to room temperature naturally. After that, the OxCNT were collected and washed with deionized water and ethanol for 3 times for further use.

In typical synthesis, 0.01 mol L^{-1} $MnCl_2$ (0.0378 g), 50 mg OxCNT and 30.0 mL formamide (FA) were mixed and sonicated for 120 minutes to get a homogeneous black suspension. Afterwards, the as-prepared precursor was transferred to autoclave and heated at different temperature, ranging from 160 ℃, 170 ℃ and 180 ℃ for 12 h. Then the as-formed brown precipitate was membrane-filtered, purified with deionized water and ethanol for 3 times and subsequently dried at 60 ℃ overnight.

1.4 Electrochemical measurements

The electrochemical measurements were performed at room temperature in a three-electrode system in 0.1M aqueous KOH solution using an electrochemical work-station (CHI 660E, Chenhua, Shanghai). Platinum electrode was utilized as the counter electrode and Saturated Calomel Electrode (SCE) was used as the reference electrode. Th prepare the working electrode, 5.0 mg Mn-NC/CNT catalyst mixed with 490 uL DMF and 10 μL 5% Nafion solution and the mixture was subsequently treated with ultrasonic for 120 minutes to form homogeneous catalyst ink. Then 5 μL catalytic ink was carefully dropped onto polished glassy carbon rotating disk electrode (RDE, diameter~5 mm) with a catalyst loading of 0.26mg cm^{-2}. Then the ink was allowed to dried naturally before submitting to electrochemical measurement station. In the alkaline solution, the electrochemical test will obey the equation that E(RHE) =

E(SCE)+ 0.767 V at 21 ℃. For the oxygen reduction reaction (ORR) test, the O_2 gas was firstly bubbled into the electrolyte for at least 30 min to form O_2 saturation. The cyclic voltammetry (CV) spectrums were collected at scan rate of 10 mV s^{-1} from -1 V to 0 V and the linear sweep voltammetry (LSV) spectrum were carried out at rotation speed of 400, 625, 900, 1225, 1600, and 2025 rpm with a scan rate of 5 mV s^{-1} from -1 V to 0 V.

1.5 Calculation Methods and Models

For the Mn-NC model, Material Studio 5.5 software package were utilized. The Mn-NC model was also used a periodic 4 × 4 graphene monolayer for the carbon framework. Subsequently, two carbon atoms were removed, followed by the substitution of four carbon atoms around the divacancy site with four nitrogen atoms to provide the anchoring site for manganese atom. All calculations were carried out with Viena Ab-initio Simulation Package (VASP) which based on density functional theory (DFT+U, the description correlation for Mn is 3.5). We replaced the inner cores by Generalized Gradient Approximation (GGA) and used the Perdew-Burke-Ernzerh (PBE)[1] of functional to describe the exchange and correlation. After fully relaxed, the bulk lattice was optimized using the 3 × 3 ×3 Monkhorst-Pack type of K-point sampling[2] and the period slab model was separated by 16 Å of vacuum, which is sufficiently large to avoid their interactions. The cut-off energy was set at 400 eV for all calculations with the energy change convergence criterion of 1×10^{-4} eV. After further optimized, atomic positions were allowed to relax until stable as well as the total energy could nearly maintain a constant which indicated the structure stayed stable with the lowest energy. Spin polarization was also considered in all the calculations including the dipole correlation.

The calculation of ORR performance on active center of various electrocatalysts were developed by Nørskov and his co-workers[3]. Followed by their computational system, the Gibbs Free Energy of f-MnNC/CNT were analyzed. In the alkaline electrolyte, the ORR proceeds a four-electron pathway and the mechanism of oxygen reduction reaction was normally adopted as follows:

$$(1)\quad O_2(g) + * + H_2O(l) + e^- \rightarrow OOH* + OH^-$$

$$(2)\quad OOH* + e^- \rightarrow O* + OH^-$$

$$(3)\quad O* + H_2O(l) + e^- \rightarrow OH* + OH^-$$

$$(4)\quad OH* + e^- \rightarrow * + OH^-$$

To be more detailed, the symbol of * stands for the active center which locate on the surface of catalytic bulk, (l) and (g) refer to liquid and gas phases, respectively and O*, OH* and OOH* are adsorbed intermediates in the procedure of electrochemical reaction. Free energy change (ΔG) from initial state to final state of the reaction can be calculated as follows:

$$(5)\quad \Delta G = \Delta E + \Delta ZPE - T\Delta S + \Delta G_U + \Delta G_{pH}$$

where ΔE is the reaction energy of reactant and product molecules adsorbed on surface of catalysts, which is obtained from DFT calculations; ΔZPE and ΔS are the changes of zero-point energies and entropy due to the reaction, respectively.[4] The $\Delta G_U = - eU$, where U stands for electrode applied potential relative to RHE and e is the elementary charge transferred. ΔG_{pH} is the correction for H^+ free energy which is determined by the reduction reaction and oxidation reaction. $\Delta G_{pH} = - k_B T \ln[H^+]$, where k_B is the Boltzmann constant and T is the temperature.

2. Supplementary figures and captions

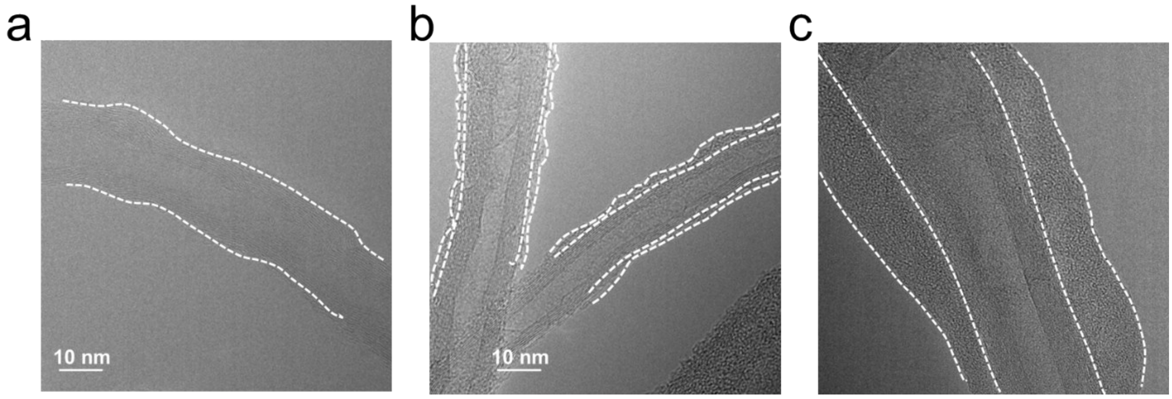

Figure S1. TEM images of (a) CNT, (b) f-MnNC/CNT-160 and (c) f-MnNC/CNT-180.

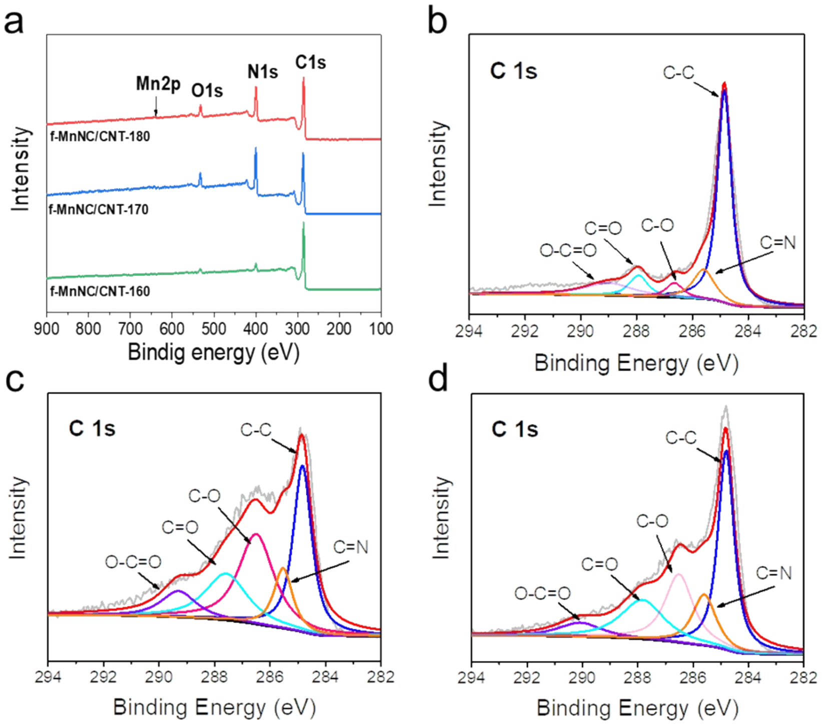

Figure S2. X-ray photoelectron spectroscopy (XPS) (a) survey and (b, c, d) C 1s spectra of f-MnNC/CNT-160, f-MnNC/CNT-170 and f-MnNC/CNT-180.

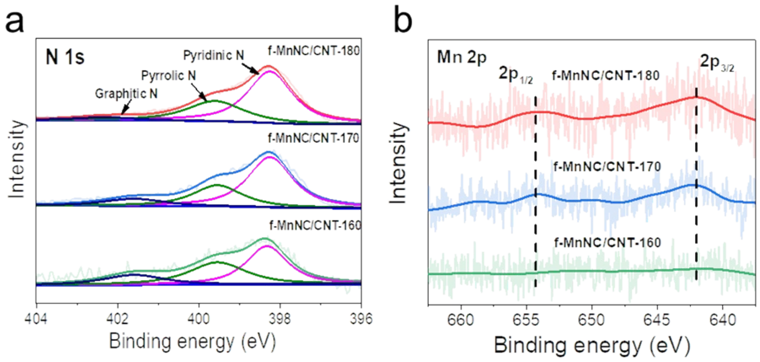

Figure S3. X-ray photoelectron spectroscopy (XPS) spectra of (a) Mn 2p and (b) N 1s of f-MnNC/CNT-160, f-MnNC/CNT-170 and f-MnNC/CNT-180.

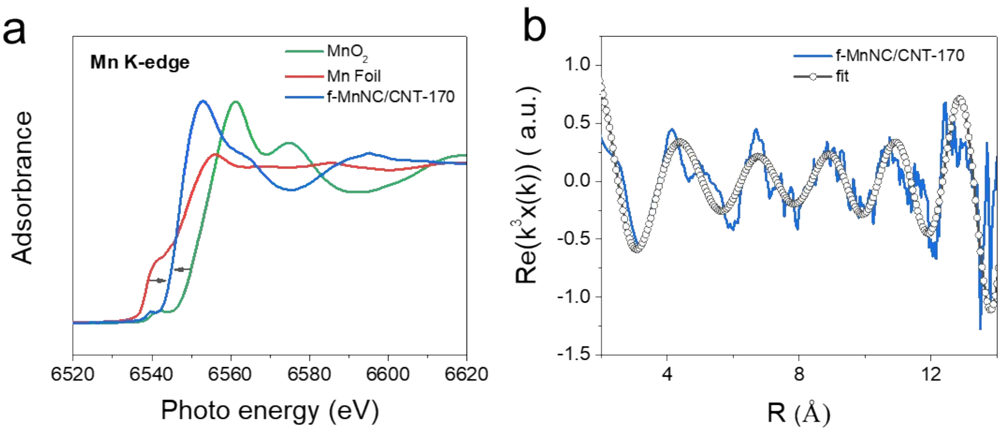

Figure S4. (a) Experimental K-edge XANES Mn spectra of f-MnNC/CNT-170 and reference samples (Mn foil and MnO_2) and (b) Mn K-edge EXAFS spectra fitting curves in k space.

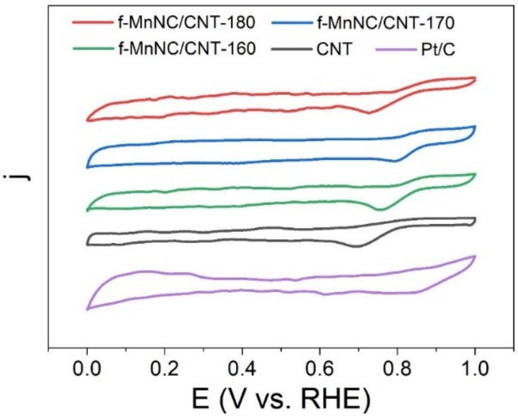

Figure S5. CV curves of f-MnNC/CNT-160, f-MnNC/CNT-170, f-MnNC/CNT-180, CNT and commercial Pt/C.

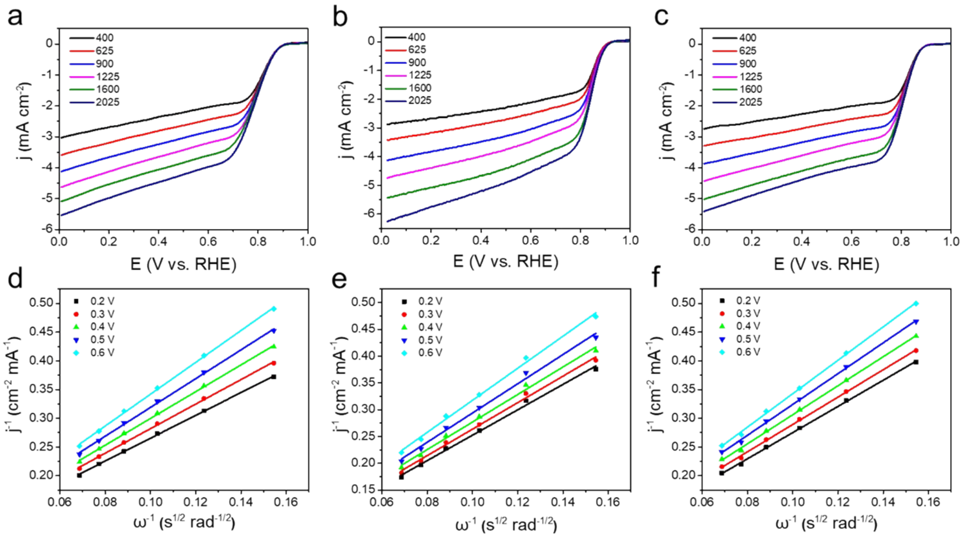

Figure S6. RDE voltammograms at different rotation speeds and corresponding Koutecky-Levich plots of (a, d) f-MnNC/CNT-160, (b, c) f-MnNC/CNT-170 and (c, f) f-MnNC/CNT-180.

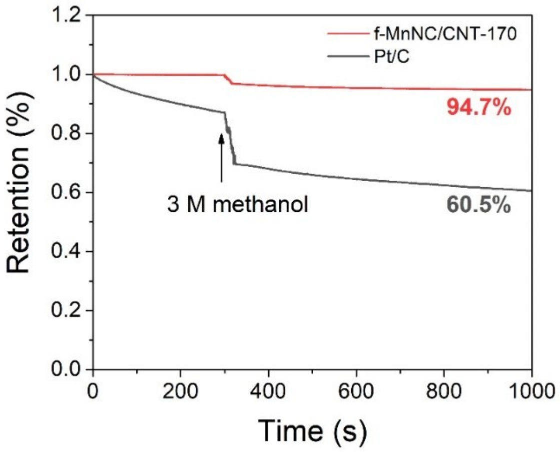

Figure S7. Crossover effect tests of f-MnNC/CNT-170 and Pt/C in 0.1 mol L^{-1} KOH electrolyte.

3. Supplementary tables

Table S1. Elements analysis of f-MnNC/CNT-160, f-MnNC/CNT-170, f-MnNC/CNT-180 characterized by XPS spectra.

Elements Samples	C (at. %)	N (at. %)	O (at. %)	Mn (at. %)
f-MnNC/CNT-160	90.07	6.95	2.72	0.27
f-MnNC/CNT-170	68.64	23.50	7.19	0.67
f-MnNC/CNT-180	73.33	21.28	4.51	0.88

Table S2. EXAFS fitting structural parameters of f-MnNC/CNT-170.

Sample	Scattering pair	CN	R(Å)	$\sigma^2(10^{-3}Å^2)$	R factor
Mn in f-MnNC/CNT-170	Mn-N	3.9	1.88	0.013	0.001

In the table, CN means the coordination number of Mn-N moiety, R is the distance between central atoms and surrounding coordinated atoms, σ^2 is Debye-Waller factor and R factor is employed estimate the fitting in R space. Error bounds that characterize the structural parameters obtained by EXAFS spectroscopy were estimated as N ± 20%; R ± 1%; σ2 ± 20%; ΔE0 ± 20%. Fe- (FT range: 2.0-10.5 $Å^{-1}$; fitting range: 0.5-3.0 Å)

Table S3. Zero point energy (eV) and entropies energy (T=298.15K) for gaseous and adsorbed intermediates.

	ZPE	TS
HO*	0.35	0.1
O*	0.07	0.06
HOO*	0.42	0.21
H_2	0.27	0.42
O_2	0.57	0.60

Reference：

1. K. Burke, M. Ernzerhof and J. P. Perdew, *Chem. Phys. Lett.*, 1997, **265**, 115-120.
2. D. J. Chadi, *Physical Review B Condensed Matter*, 1977, **16**, 5188--5192.
3. J. K. Norskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J. R. Kitchin, T. Bligaard and H. Jonsson, *J. Phys. Chem. B*, 2004, **108**, 17886-17892.
4. H. Xu, D. Cheng, D. Cao and X. C. Zeng, *Nat. Catal.*, 2018, **1**, 339-348.