Enhancing the catalytic activity of the MnNC catalyst by regulating the coordination environment

Wang Wang[b], Yucheng Liu[a]*

[a]Core Facility of Wuhan University, Wuhan University, Wuhan 430072, China. Email: lyc2015@whu.edu.cn

[b]College of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China.

Experimental Section/Methods

Synthesis of MnNC: 1 g 2-methylimidazole (Aladdin, 98%), 0.05 g $MnCl_2$ (Sinopharm Chemical Reagent Co., Ltd.) and 0.15 g EC300J (Carbon black) was mixed in 30 mL ultrapure water and stirred vigorously for 24 h. Then, the mixed solution was evaporated using the rotary evaporation equipment to obtain the black mixture powder. Subsequently, the powder was annealed at 900 °C for 2 h under Ar atmosphere. After cooling to room temperature, the sample was washed with 3 M HCl (Sinopharm Chemical Reagent Co., Ltd.) at 90 °C for 12 h to obtain MnNC.

Synthesis of MnNC-O: 0.2 g EC300J (Carbon black) was dispersed in 40 mL 12 mol/L nitric acid and maintained at 80 °C for 6 h (12 h for the preparation of MnNC-O2, 24 h for the preparation of MnNC-O3). After washing and drying, 0.15 g of the obtained oxidized carbon black, 0.05 g $MnCl_2$ and 1 g 2-methylimidazole were mixed in 30 mL ultrapure water and stirred vigorously for 24 h. Then, the mixed solution was evaporated using the rotary evaporation equipment to obtain the black mixture powder. Subsequently, the powder was annealed at 900 °C for 2 h under Ar atmosphere. After cooling to room temperature, the sample was washed with 3 M HCl at 90 °C for 12 h to obtain MnNC-O1. For MnNC-O2 and MnNC-O3, the oxidizing time of the carbon black was 12 h and 24 h, respectively. The other procedures are the same as the preparation of MnNC-O1.

Structure and morphology characterization: Powder X-ray diffraction (XRD) patterns were performed on a SmartLab with a Cu Kα radiation source. High-angle annular dark-field-TEM (HAADF-TEM), and element mapping images were obtained from a Titan G2 60–300 microscope. The ACHAADF-STEM images were collected from a JEM ARM300F microscope with a probe-forming spherical aberration corrector. X-ray photoelectron spectroscopy (XPS) measurement was carried out with a Thermo Fischer Nexsa spectrophotometer. All the binding energies are corrected by the C 1s peak of 284.5 eV. The surface area was analyzed from N_2 adsorption-desorption isotherms at liquid nitrogen temperature (77 K) using an ASAP 2460 Surface Area and Porosity Analyzer. The specific surface area and pore distribution were analyzed based on Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model, respectively. Inductively coupled plasma atomic emission spectrometry (ICP-AES) was conducted by a plasma spectrometer (Agilent 5110).

Preparation of working electrodes: To make the working electrode, 2.5 mg of the catalyst was dispersed in a solution of 0.49 mL of isopropyl alcohol mixed with 0.01 mL of 5 wt% Nafion solution and then sonicated for at least 2h. The rotating ring-disk Electrode (RRDE) was polished with 1.0, 0.5, and 0.05μm alumina powder successively to obtain a mirror-like surface and then washed with ultrapure water and ethanol with sonication. After the RRDE was dried in air, 30 μL of the ink was dropped on the surface of the RRDE by spin coating method (loading= 0.6 mg/cm²). Electrochemical measurements were taken after the ink on the

electrodes had dried in the air.

Electrochemical Measurements: The electrochemical properties of all samples were measured by using a CHI 760E electrochemical analyzer (CH Instruments, Chenhua Co., Shanghai) in a three-electrode system at $30 \pm 1°C$. The modified RRDE with various catalyst samples, saturated calomel electrode and a graphite rod were used as the working electrode, reference electrode, and counter electrode, respectively. The potentials were reported with respect to the reversible hydrogen electrode (RHE). The RRDE curves were recorded under 1600 rpm at a scan rate of 5 mV/s for ORR in 0.1 M oxygen-saturated $HClO_4$ and KOH solution.

In this work, the selectivity for the electrochemical synthesis of H_2O_2 is the mole fraction selectivity. Mole fraction selectivity $X_{H_2O_2}$ is defined by the following equation:

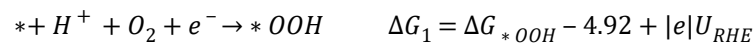$$X_{H_2O_2} = \frac{n(H_2O_2)}{n(H_2O_2) + n(H_2O)}$$

$$= \frac{\frac{I_R}{N}\Big/ 2F}{\frac{I_R}{N}\Big/ 2F + (I_D - \frac{I_R}{N})\Big/ 4F}$$

$$= \frac{2I_R/N}{I_D + I_R/N}$$

Where I_R, I_D, N and F are the ring current, disc current, collection efficiency of the setup and Faraday constant, respectively.

DFT computational calculation details: Geometry optimization and total energy calculations in this article were performed with the generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof (PBE) and spin-polarization was considered in all the calculations. A plane-wave energy cut-off of 500 eV was used in the expansion of the electronic wave function and the convergence threshold was 10^{-5} eV in energy and 0.005 eV/ Å in force for electronic relaxation and ion relaxation, respectively. Density of K point was set 0.04 Å^{-1} with gamma method, in which KPOINTS file was constructed by VASPKIT. The vacuum space of the model in the article was set 15 Å. All the atoms in these structures were allowed to relax while geometry optimization. The computational hydrogen electrode (CHE) model which used half of the chemical potential of H_2 instead of the chemical potential of H^+ was used to Proton-coupled electron transfer (PCET) thermodynamics of the oxygen evolution reactions in these structures. The entropies and zero-point-energies (ZPE) of H_2 molecule, H_2O molecule and ZPE of adsorbed oxygenated species (*O_xH_y) which * means adsorption site was referred to the literature.[1] Thus, the reaction free energy (ΔG) can be calculation by the following equation:

$$\Delta G = \Delta E + ZPE - T\Delta S + \Delta G_U$$

The overall reaction scheme of 2e⁻ ORR process in acid condition and its reaction free energy which follows formation energy approach can be described as follows:

$$*+ H^+ + O_2 + e^- \rightarrow *OOH \qquad \Delta G_1 = \Delta G_{*OOH} - 4.92 + |e|U_{RHE}$$

$$*OOH + H^+ + e^- \rightarrow *+ H_2O_2 \qquad \Delta G_2 = \Delta G_{H_2O_2} - \Delta G_{*OOH} + |e|U_{RHE}$$

ΔG_{*OOH} means adsorption energy of OOH. $\Delta G_{H_2O_2}$ can be described as follows:

$$\Delta G_{H_2O_2} = \Delta G_{f,H_2O_2}^0 + 4.92 = 3.52$$

ΔG_f^0 means the standard Gibbs free energy of formation.
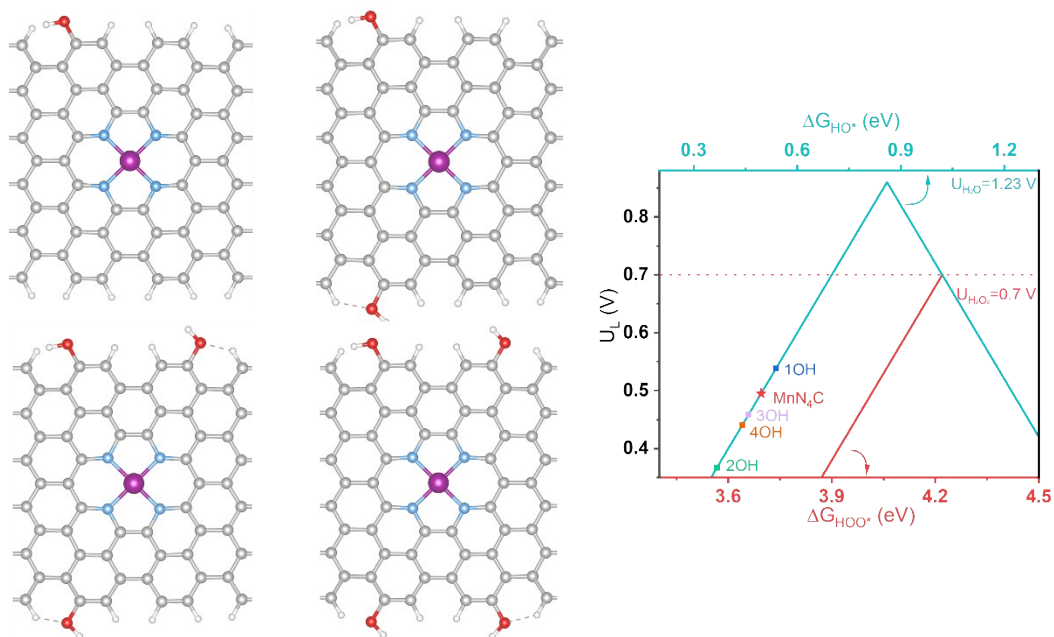
Figure S1. The structure models and the corresponding activity volcano of the MnN$_4$C sites with the introduction of OH groups.
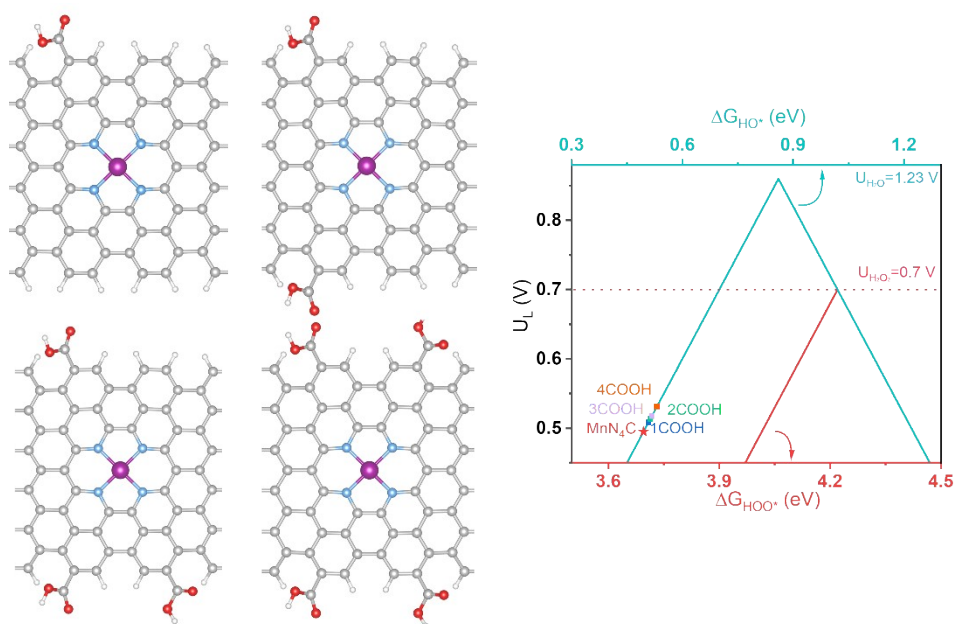

Figure S2. The structure models and the corresponding activity volcano of the MnN$_4$C sites with the introduction of COOH groups.
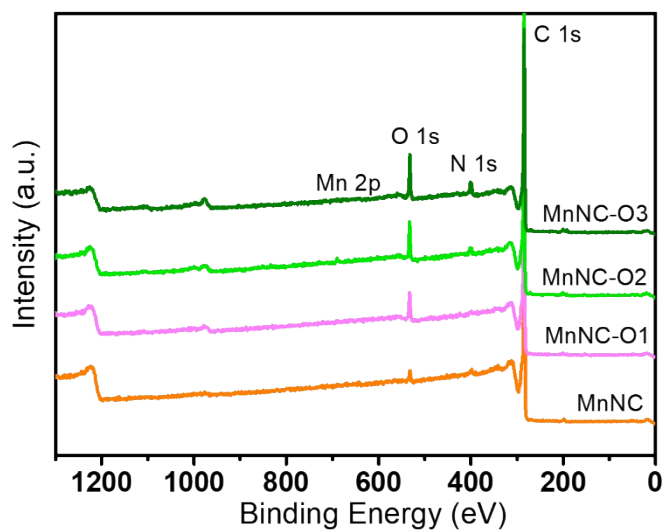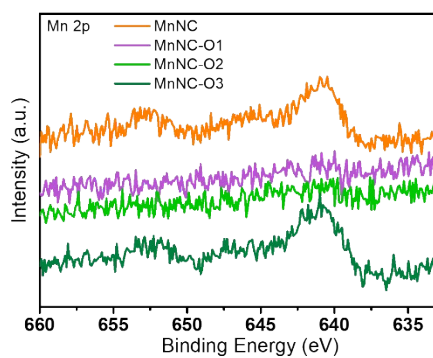
Figure S3. The XPS survey of the catalysts.

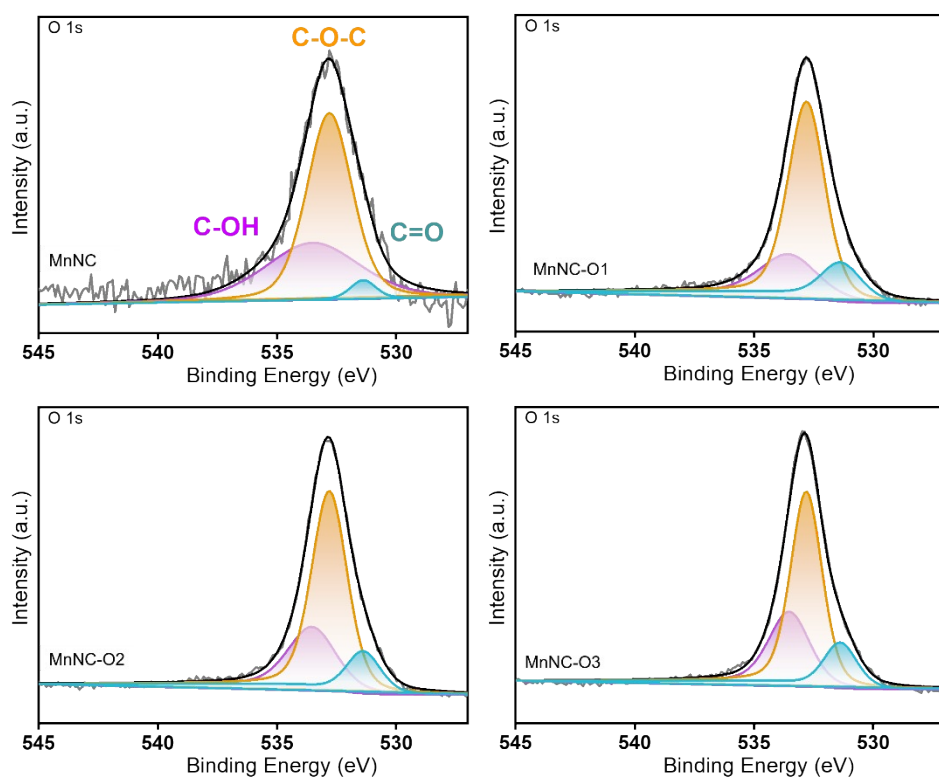Figure S4. The high-resolution Mn 2p spectra.

Figure S5. The deconvolution of the XPS high resolution O 1s spectra of the catalysts.
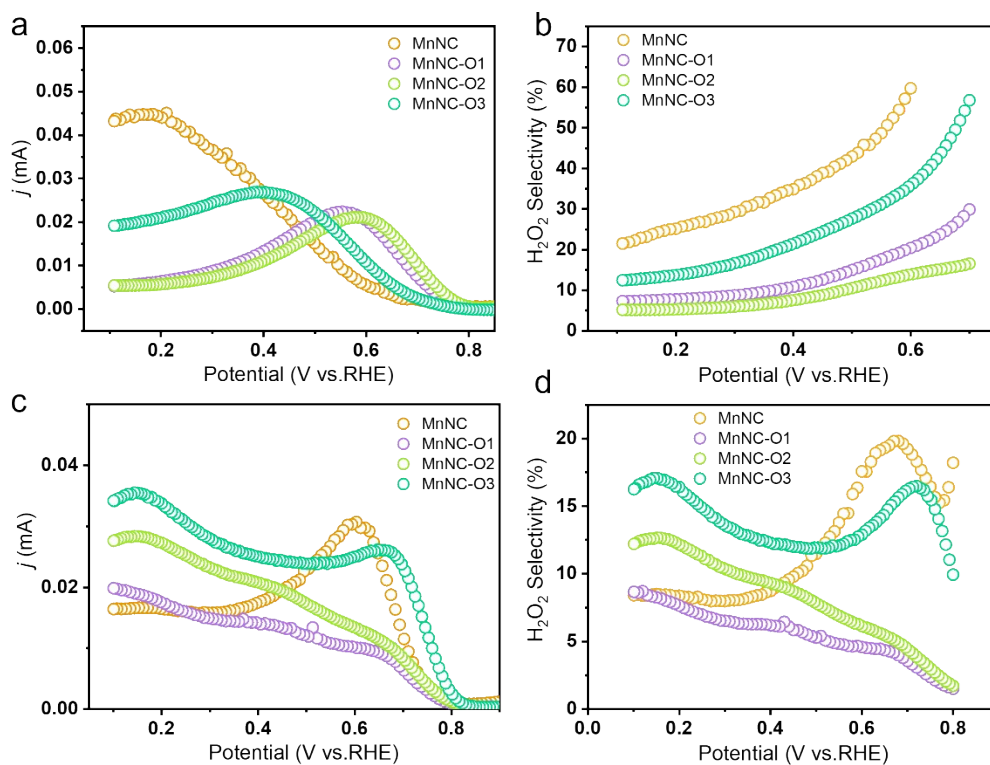
Figure S6. the ring current (a) and H_2O_2 selectivity (b) of the catalysts in 0.1 M $HClO_4$, the ring current (c) and H_2O_2 selectivity (d) of the catalysts in 0.1 M KOH.
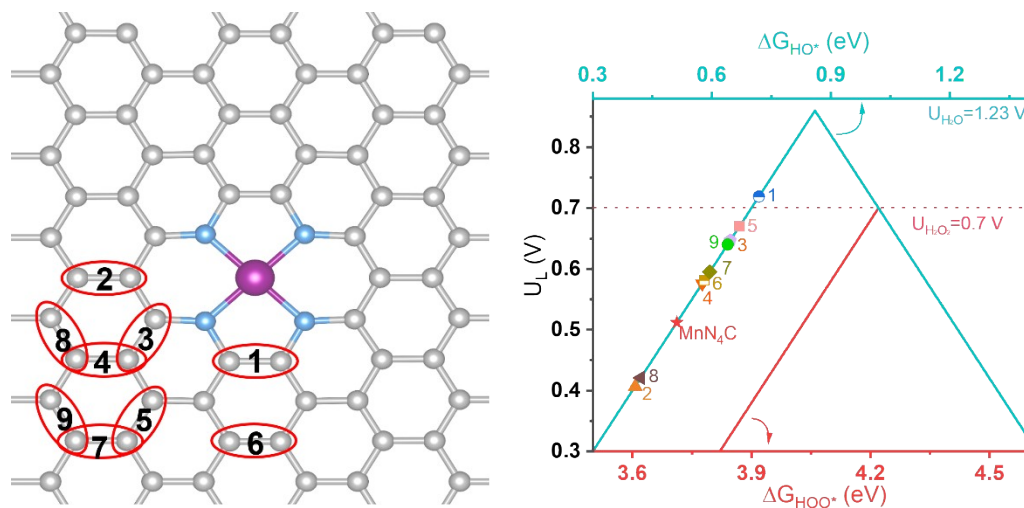

Figure S7. The structure models and the corresponding activity volcano of the MnN_4C sites with the introduction of epoxy groups at different locations.

Table S1. The atomic content of the elements in the catalysts determined by XPS

Elements	Atomic content (at%)			
	MnNC	MnNC-O1	MnNC-O2	MnNC-O3
C	96.14	93.67	91.58	86.64
Mn	0.18	0.07	0.07	0.23
N	1.47	1.32	2.47	5.42
O	2.21	4.94	5.88	7.71

Reference

1.   M. Sprik and G. Ciccotti, *The Journal of Chemical Physics*, 1998, **109**, 7737-7744.