

Supporting Information

Adjusted MnO oxygen vacancy for highly selective ORR production of H₂O₂

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Experimental Section

Chemicals

Potassium permanganate (KMnO₄) is purchased from Sigma-Aldrich (Shanghai) Co., Ltd. Manganese (II) Sulfate Monohydrate (MnSO₄·H₂O), Potassium hydroxide (KOH), Sul-furic acid (H₂SO₄), Cerium (IV) sulfate tetrahydrate (CeSO₄·4H₂O), are all purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd, located in China. Acetylene black (C) is obtained from Sinopharm Chemical Reagent Co., Ltd, China. All reagents were utilized without undergoing additional purification. For all the experiments, ultrapure water (Millipore, 18.25 MΩ cm⁻¹) was utilized.

Catalyst preparation.

Typically, 4.9575 g of KMnO₄ and 1.68 g of MnSO₄ were dissolved in 25 mL of ultrapure water. Then, the two solutions were mixed and heated and stirred in a water bath at 80°C for 2 h. After that, it was transferred to a reactor and placed in an oven for a hydrothermal reaction for 10 h, with the temperature at 180°C. After the reactor was completely cooled down, the sample was removed and washed by filtration with a large

amount of ultrapure water, and then dried at 60°C overnight, and then recycled after grinding the sample, which was labeled as MnO₂-180.

200 mg of MnO₂-180 catalyst was weighed and calcined in a tube furnace under 10% hydrogen-argon atmosphere with a calcination temperature interval of 250°C-850°C, a temperature gradient of 100°C, a reduction time of 2 h, and a ramp rate of 5°C/min.

The samples were labeled as MnO-temperature. Then an equal amount of MnO₂-180 was weighed and the reduction temperature was controlled to be 550 °C. The samples were calcined for 0.5 h, 1 h, 2 h and 3 h. The samples were labeled as MnO-550-time.

Electrochemical performance tests

The potentials obtained from the electrochemical tests in the experiment were all converted by the following equation

$$E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \cdot \text{pH} + 0.197$$

The electrolytes used for the experimental tests were all 0.1 M KOH solution at a concentration of 0.1 M KOH, pH = 12.7.

Preparation of working electrodes

Take 5 mg catalyst and 1 mg Vulcan XC-72 toner, add them to a mixture of 500 µl of isopropanol, 480 µl of water and 20 µl of nafion solution, sonicate for 1 h until well mixed, and configure the dispersion. Use a pipette gun to measure 10 µl of the dispersion onto the disk electrode, dry naturally and then test.

Electrochemical test

The electrochemical tests were performed using a three-electrode system, with the reference electrode as Ag/AgCl electrode, the counter electrode as graphite rod, and the working electrode as rotating ring disk electrode (RRDE), with the acquisition coefficient of the rotating ring disk electrode being 0.37. The voltage range of the LSV test was 0.5 mV, and that of the LSV test was 0.5 mV.

The voltage range for the LSV test was 0 to 1.2 V vs RHE, the rotational speed was

1600 r.m.p. The applied decomposition voltage was 1.3 V vs RHE constant voltage decomposition of hydrogen peroxide in order to detect the production of hydrogen peroxide. The H₂O₂ yield and the number of electrons in ORR were calculated by the following equations.

Formula for calculating selectivity

$$\text{Selectivity (\%)} = \frac{200I_r}{NI_d + I_r}$$

Formula for calculating electron transfer number

$$n = \frac{4I_d N}{NI_d + I_r}$$

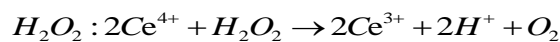
Formula for calculating Faraday's efficiency

$$FE(\%) = \frac{100 \times I_r}{NI_d}$$

I_r is the ring current, I_d is the disk current, and N is the collection factor of the ring electrode.

2.3.4 Hydrogen peroxide yield test

Hydrogen peroxide yield was tested in an H-type electrolytic cell with Nafion membrane as the isolation membrane, and the test was carried out under the I-t mode test with the constant voltage set to 0.1 V, 0.3 V, 0.5 V vs RHE, and each time at an interval of 1 h. 200 μl of the electrolyte was taken, and added into 1.8 ml of Ce(SO₄)₂ standard solution of a concentration of 0.25 mM, and mixed thoroughly to make a After fully reacted, it was poured into a cuvette and its absorption was tested at 200 ~ 400 nm band using a UV-visible photometer. The standard curve can calculate the concentration of hydrogen peroxide. The reaction formula of hydrogen peroxide and cerium sulfate is:



The Faraday efficiency of hydrogen peroxide can be calculated by the following equation Formula for calculating Faraday efficiency:

$$FE(\%) = \frac{2CFV}{Q}$$

C is the concentration of H_2O_2 ($\text{mol}\cdot\text{L}^{-1}$), V is the volume of electrolyte (L), F is Faraday's constant ($96485 \text{ C}\cdot\text{mol}^{-1}$), and Q is the charge consumed by the reaction (C). The electrochemical workstation used for all electrochemical tests conducted in this work was CH 760e.

Table S1 The ratio of the peak area of facet (200) to that of facet (111) of MnO catalysts obtained at different calcination temperatures.

Catalyst	ratio
MnO-250	1.41
MnO-350	1.48
MnO-450	1.52
MnO-550	1.55
MnO-650	1.52
MnO-750	1.50
MnO-850	1.48

Table S2 The ratio of the peak area of facet (200) to that of facet (111) of MnO catalysts obtained at different reduction times.

Catalyst	ratio
MnO-550-0.5h	1.53
MnO-550-1h	1.52
MnO-550-2h	1.55
MnO-550-3h	1.55

Table S3 The $2e^-$ ORR selectivity of various catalysts.

Catalyst	Selectivity	doi
MnO-550-2h	98%	This work
Ni Graphene-supported	94%	10.1021/acsami.0c01278
Cu/NCNSs	81%	10.1016/j.apcatb.2022.122218
P-Ni/MC	95%	10.1016/j.cej.2021.133651

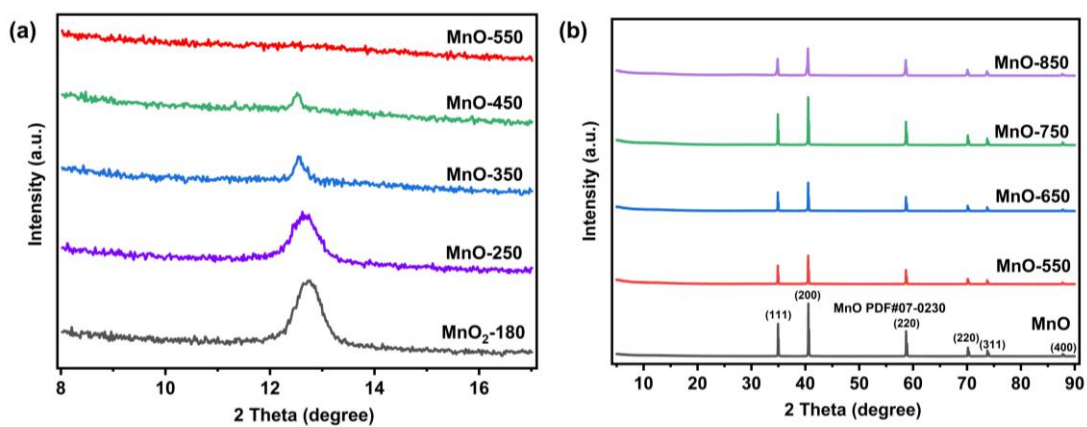


Fig.S1 XRD patterns of (a) local enlargement in Fig. 1a; (b) the pure MnO and the MnO catalyst reduced at 550 °C to 850 °C for 2 h.

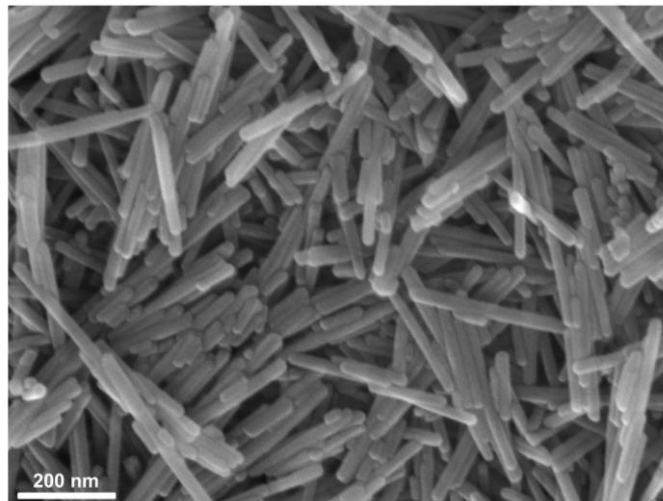


Fig. S2 SEM image of MnO₂ (synthesized at 180 °C).

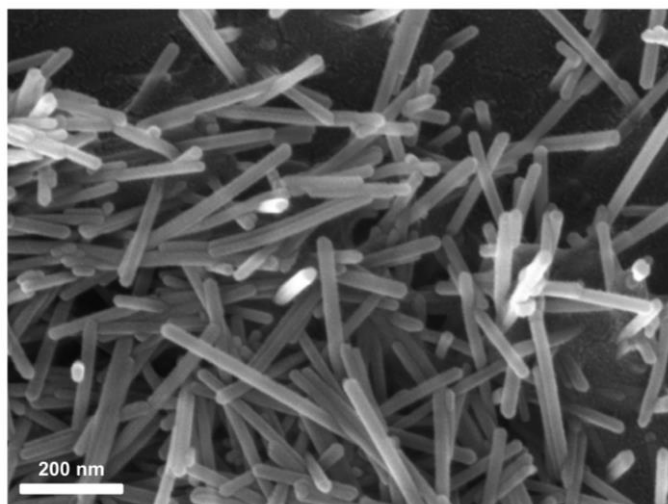


Fig. S3 SEM image of catalyst MnO (synthesized at 250 °C).

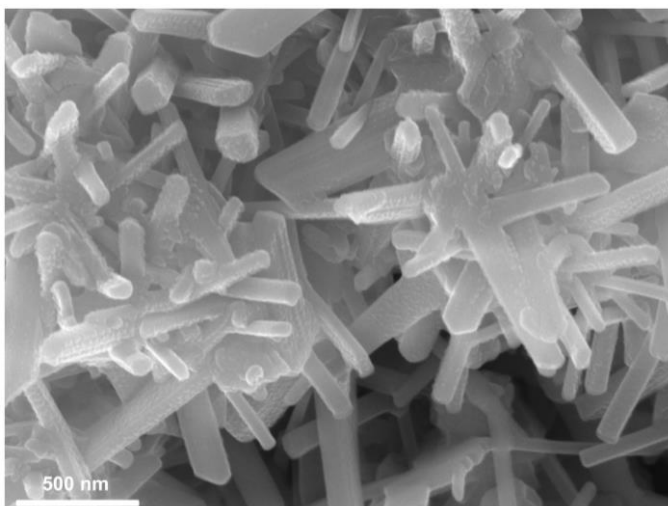


Fig. S4 SEM image of catalyst MnO (synthesized at 350 °C).

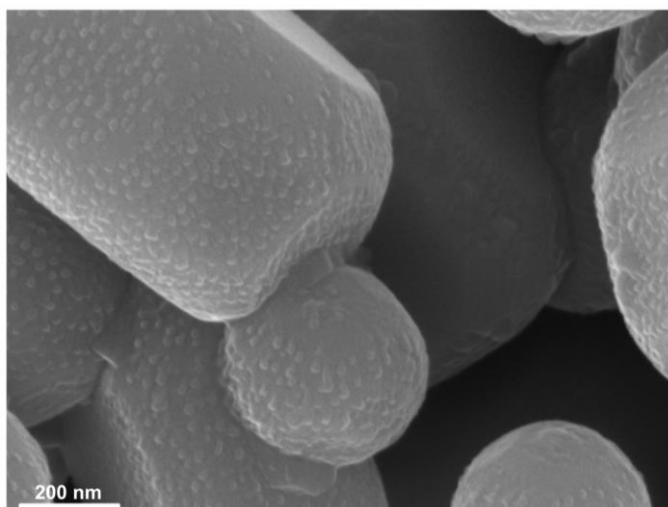


Fig. S5 SEM image of catalyst MnO (synthesized at 450 °C).

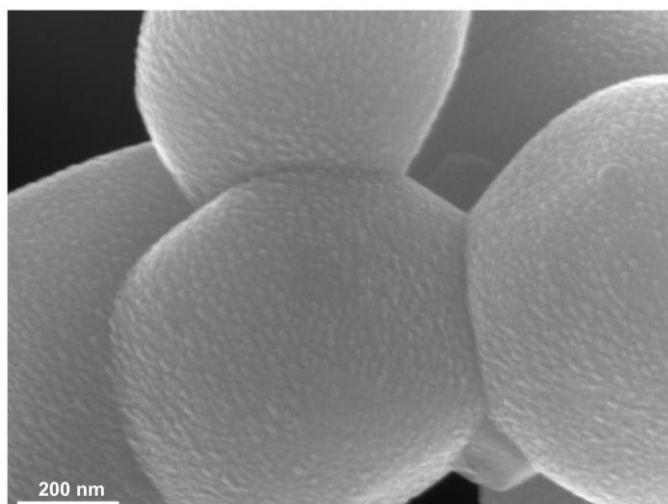


Fig. S6 SEM image of catalyst MnO (synthesized at 550 °C).

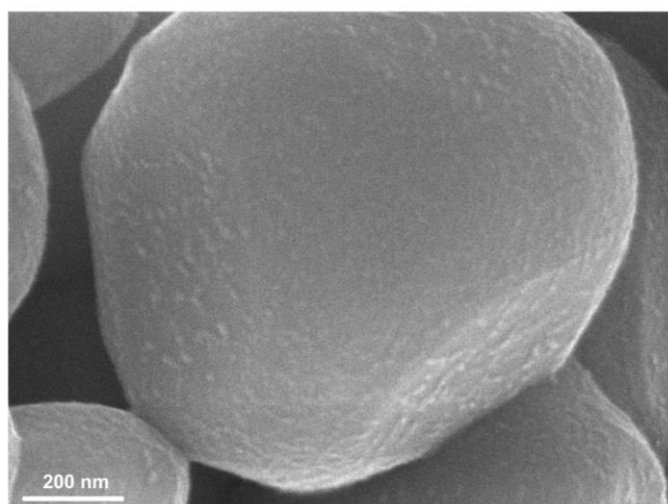


Fig. S7 SEM image of catalyst MnO (synthesized at 650 °C).

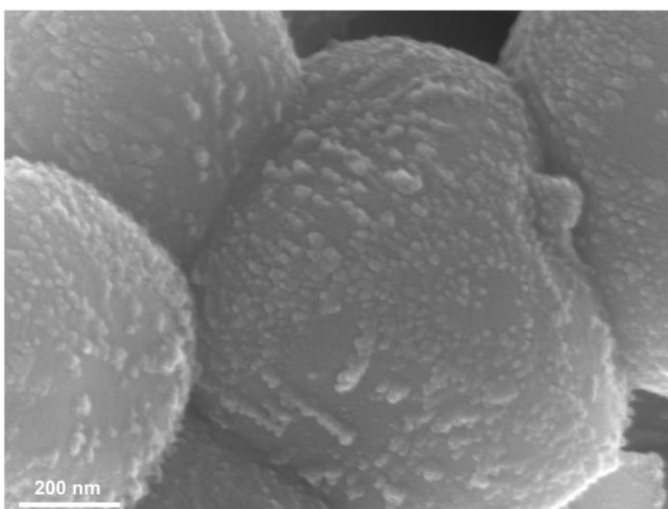


Fig. S8 SEM image of catalyst MnO (synthesized at 750 °C).

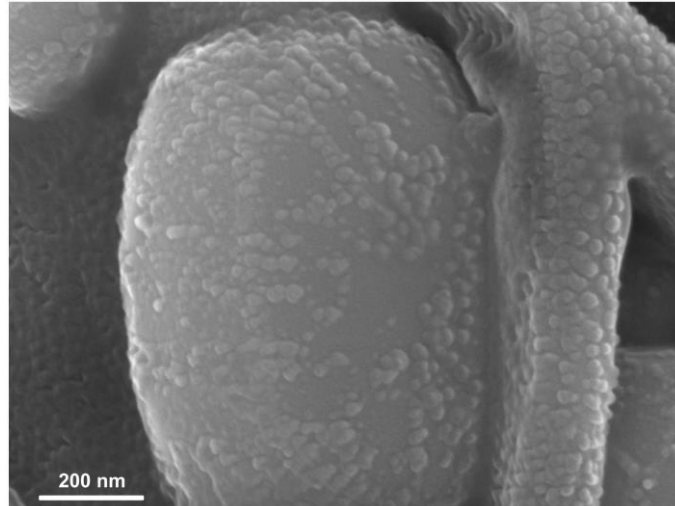


Fig. S9 SEM image of catalyst MnO (synthesized at 850 °C).

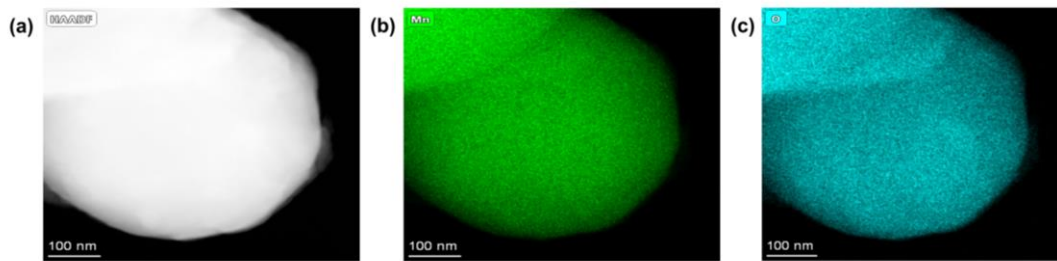


Fig. S10 (a) HAADF image of MnO-550-2h catalyst; (b) Mn elemental distribution of MnO-550-2h catalyst; (c) O elemental distribution of MnO-550-2h catalyst;

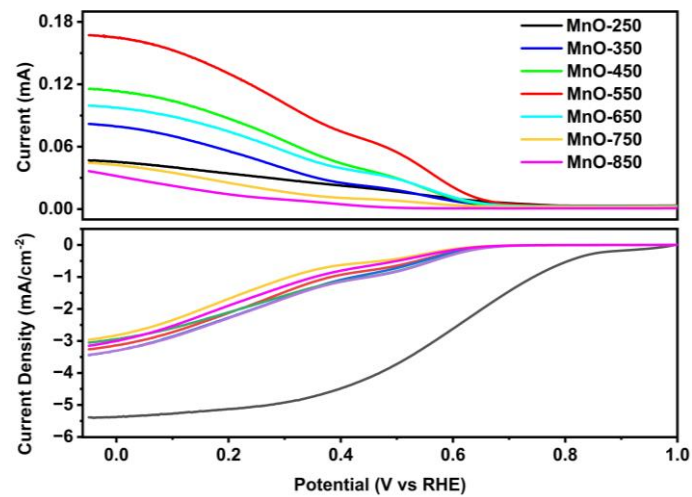


Fig. S11 LSV test of MnO catalysts reduced for 2h at different reduction temperatures.

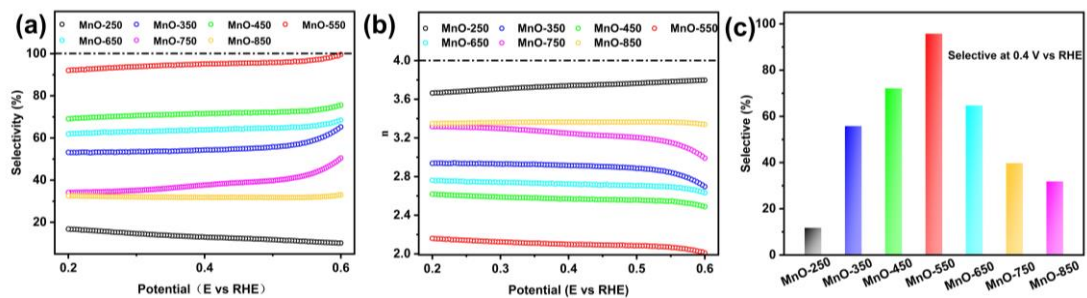


Fig. S12 (a) selectivity of MnO catalysts reduced for 2h at different reduction temperatures; (b) transferred electron number of MnO catalysts reduced for 2h at different reduction temperatures; (c) selectivity of MnO catalysts reduced for 2h at 0.4 V at different reduction temperatures;

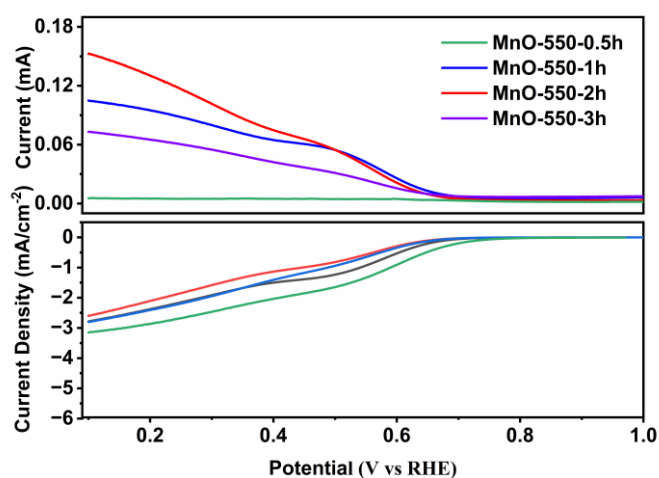


Fig. S13 LSV curves of MnO-550-0.5h, MnO-550-1h, MnO-550-2h, MnO-550-3h.

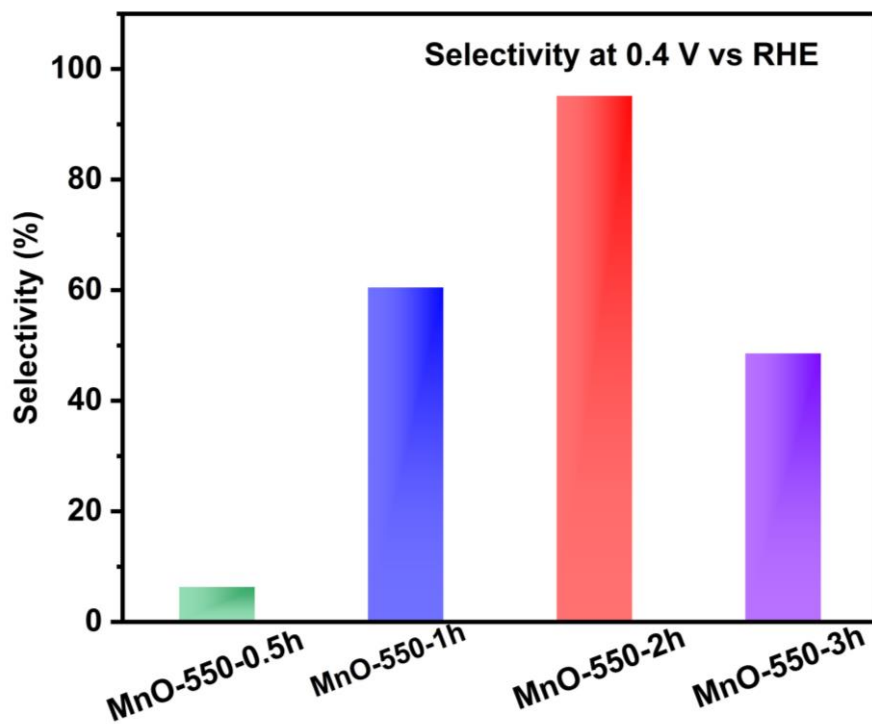


Fig. S14 Selectivity of the above catalysts at 0.4V vs RHE.

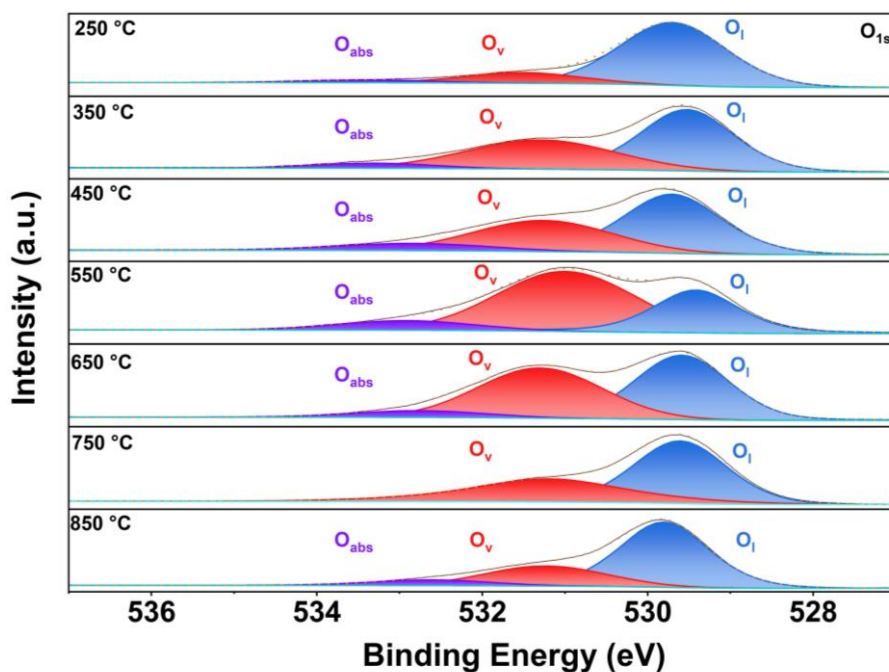


Fig. S15 O 1s XPS profiles of MnO catalysts reduced for 2 h at different reduction temperatures.

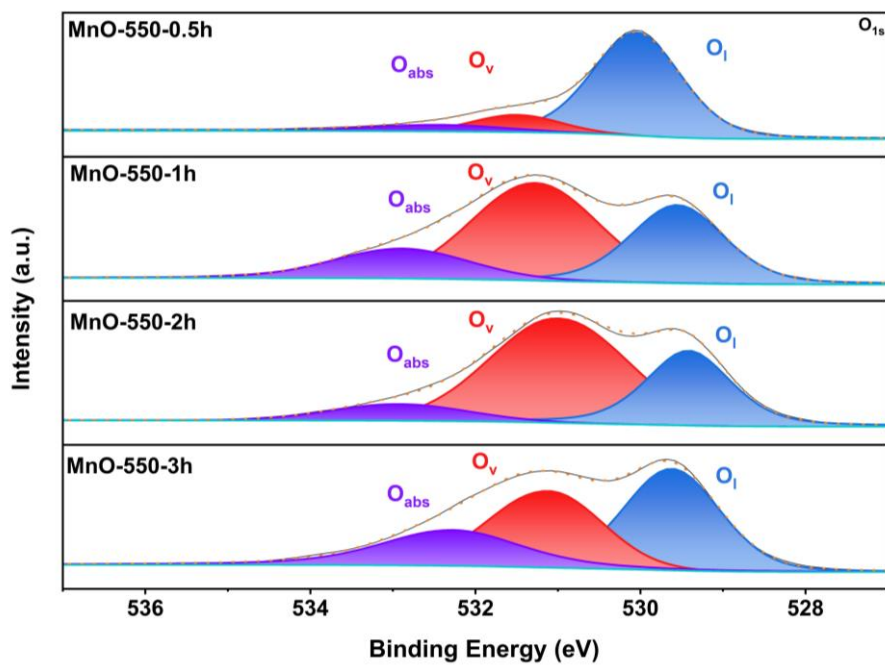


Fig. S16 O 1s XPS profiles of MnO catalysts reduced for different time at 550 °C.

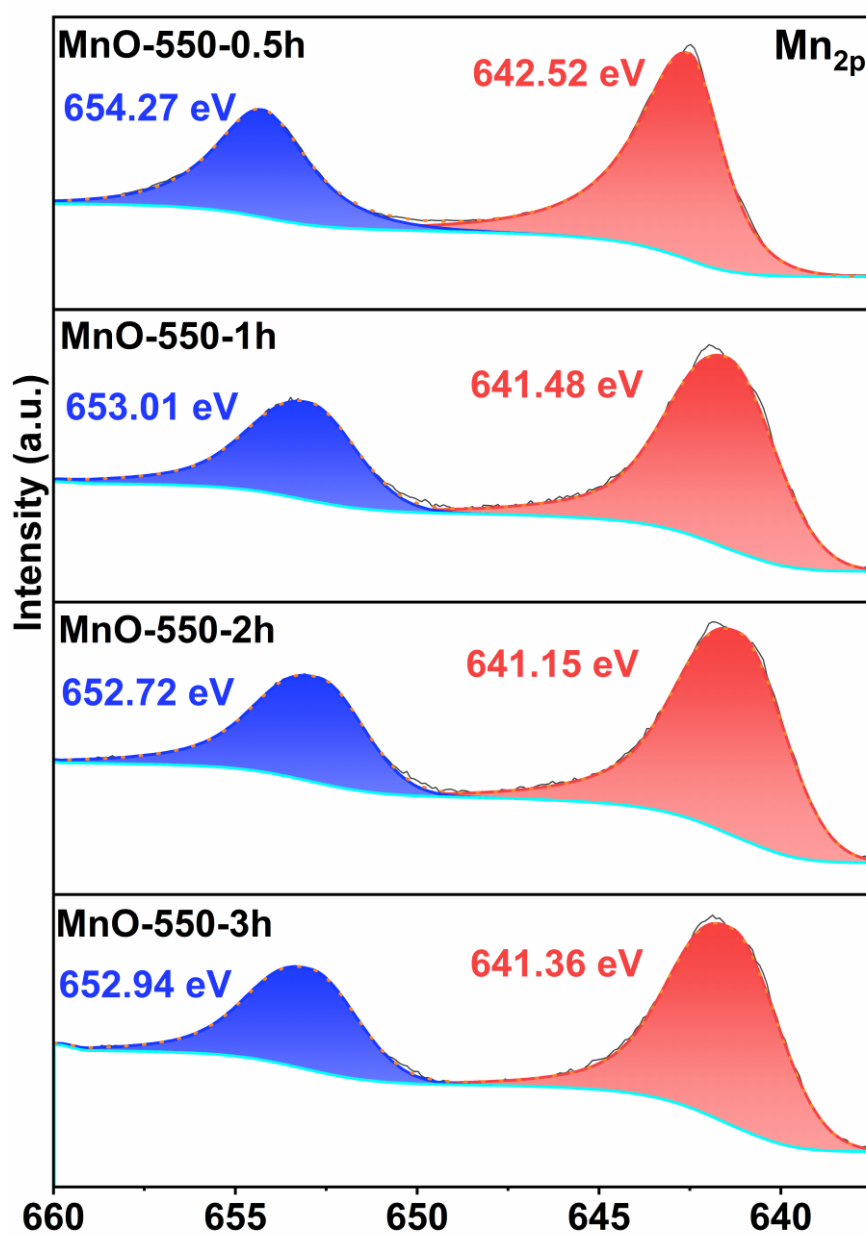


Fig. S17 Mn 2p XPS spectra of MnO catalysts obtained at different reduction times

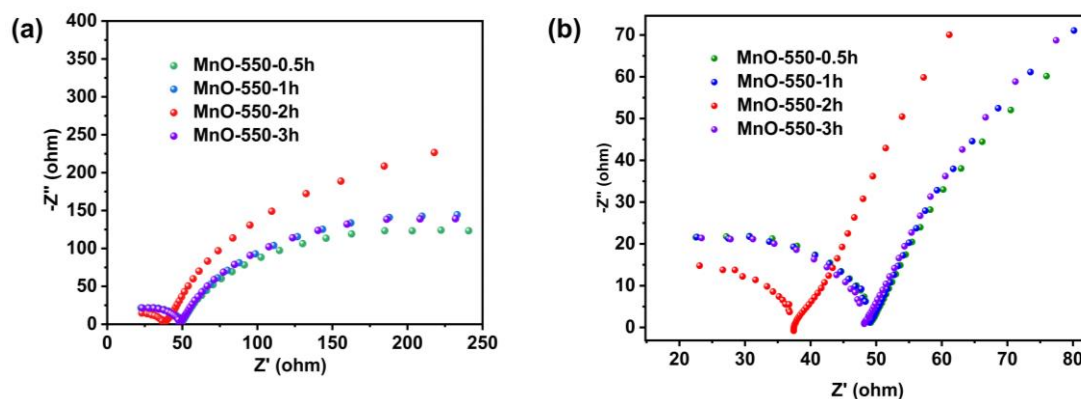


Fig. S18 (a) EIS curves of MnO catalysts obtained at different reduction times; (b) Localized enlarged figure of (a)

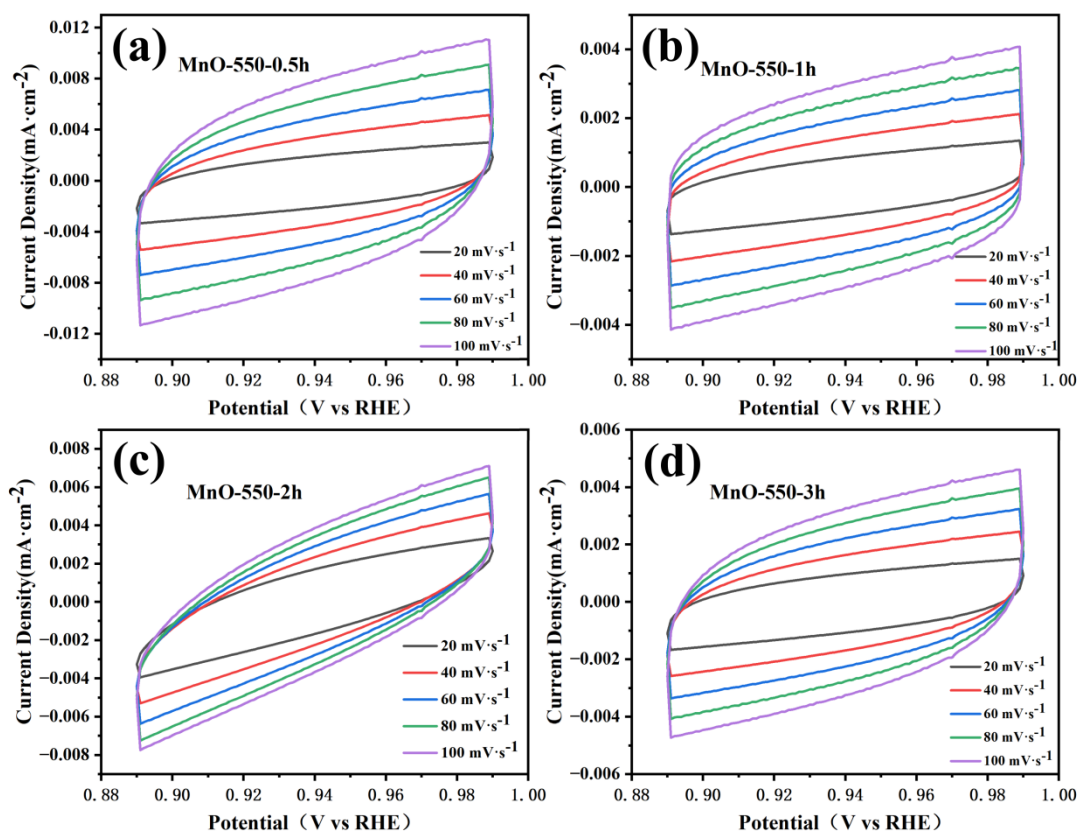


Fig. S19 (a) CV curves of MnO-550-0.5h in the non-Faraday potential window; (b) CV curves of MnO-550-1h in the non-Faraday potential window; (c) CV curves of MnO-550-2h in the non-Faraday potential window; (d) CV curves of MnO-550-3h in the non-Faraday potential window

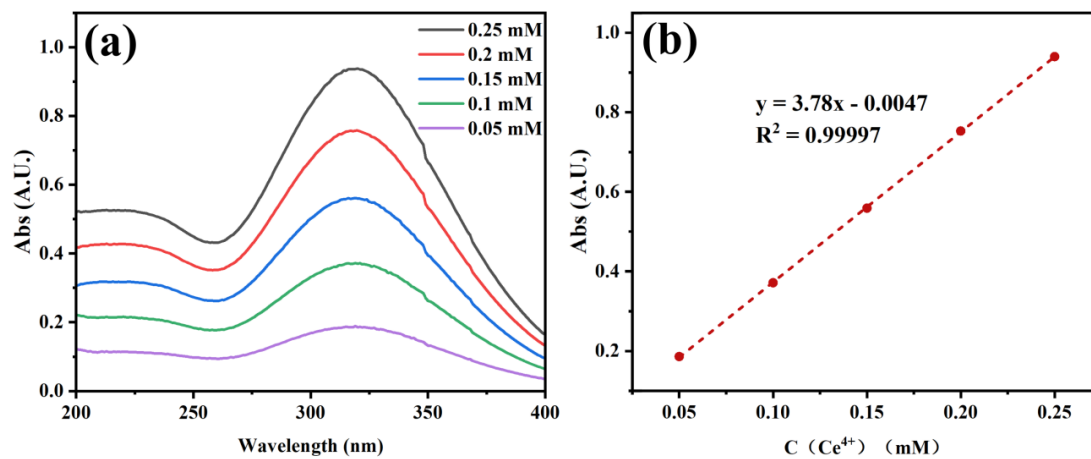


Fig. S20 (a) Absorbance spectra of standard solutions of Ce^{4+} at different concentrations; (b) standard fitting curve for Ce^{4+} . The fitted equation was $3.78x - 0.0047$, with a confidence factor R^2 of 0.99997.

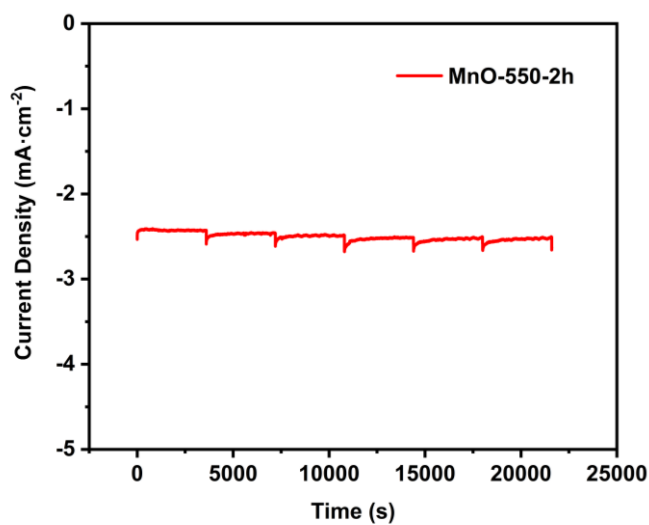


Fig. S21 I-t diagram of MnO-550-2h catalyst at 0.1 V vs RHE.

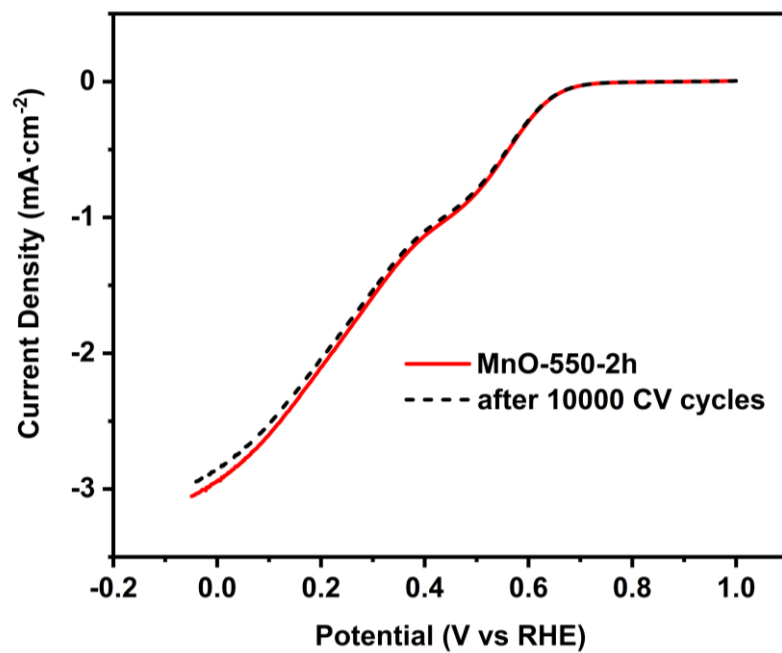


Fig. S22 Comparison of LSV after 10,000 CV cycles of MnO-550-2h.