Supporting Information

In-situ precise anchoring of Pt single atoms in spinel Mn_3O_4 for highly efficient hydrogen evolution reaction

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1. Materials

Chloroplatinic acid hexahydrate (H₂PtCl₆·6H₂O, 37.5%) was purchased from Shanghai Aladdin Biochemical Technology Co., Ltd. NF was bought from Kunshan Guangjiayuan New Materials Co., Ltd. Na₂SO₄, KOH and Mn (CH₃COO)₂•4H₂O were purchased from FUCHEN (Tianjin) Chemical Reagent Co., Ltd. CH₃COONH₄ were purchased from DAMAO (Tianjin) Chemical Reagent Factory. Benchmark 20 wt% Pt/C (commercial) catalyst were purchased from Suzhou Yilongsheng Energy Technology Co., Ltd.

2. Preparation of electrocatalysts

2.1 Synthesis of Mn₃O₄/NF

As shown in Figure S1, Mn_3O_4/NF precursor samples were prepared by electrodeposition. The details are as follows: 0.01 M Mn (CH₃COO)₂•4H₂O, 0.02 M CH₃COONH₄, and 50 mL DMSO were dissolved in 500 mL deionized water, shaken well, and set aside. NF (4 cm × 1 cm × 1 mm) was washed successively by ethanol and acetone at 1:1 volume ratio, 1.5 M HCl, and deionized water for 15 min, respectively. Then, it was washed with ethanol and dried. The 25 mL electrolyte was transferred to a three-port electrolytic cell and lasted for 60 min at a constant current of 2.0 mA at 70°C. It was washed with deionized water and dried at room temperature to obtain MnO₂/NF. Finally, the as-prepared MnO₂/NF was wetted with ethanol and calcined under 300°C for 2h in an Ar atmosphere with a heating rate of 5°C/min to form Mn₃O₄/NF.

2.2 Synthesis of Pt_{SA}-Mn₃O₄

The Pt_{SA} - Mn_3O_4 was synthesized by an electrochemical vacancy manufacturing and atom embedding strategy, which uses CHI 760E electrochemical workstation (Shanghai CH Instruments, Inc.) and a conventional three-electrode cell with 0.5 M Na₂SO₄(containing 0.095)

mM H₂PtCl₆•6H₂O). The volume of the solution in the electrolytic cell was 44 mL, Mn_3O_4/NF , graphite carbon rod, and saturated calomel electrode were used as the WE, CE, and RE, respectively. To perform 100, 300, 500, 700, and 900 potential cycles between -0.3 V *vs*. SCE and 0.5 V *vs*. SCE at a scan rate of 0.1 V s⁻¹.

3. Characterization

Scanning electron microscope (SEM), model JEOL JSM-7600F, along with transmission electron microscope (TEM), model JEOL 2100F, were used to analyze the morphology and microstructure of the as-prepared samples. HAADF-STEM images, and STEM-EDS mapping images were obtained by on a ThermoFisher Themis Z microscope equipped with two aberration correctors under 300 kV and 4 in-column Super-X detectors. The crystal structure of the catalysts was analyzed by X-ray diffraction (XRD) worked at 40 kV and 120 mA with a Cu K α radiation source ($\lambda = 1.5418$ Å) in a 2 θ angular range of 5-80°. Raman spectra were recorded on a Lab RAM ARAMIS Raman spectrometer (HORIBA Jobin Yvon) and a 514 nm laser acted as an excitation source. XPS was performed on Thermo ESCALAB 250XI spectrometer equipped with an Al K α monochromatic. UPS was performed on ThermoFisher NexsaI spectrometer equipped. ICP-OES was performed on Agilent 720ES. ESR was performed on BRUKE EMXPLUS. The EXAFS measurement of the Pt_{SA}-Mn₃O₄i at the Pt *L*₃-edge was performed at the Singapore Synchrotron Light Source (SSLS) center. Pt foil and PtO₂ were used as references. Data analysis and fitting were performed with Athena and Artemis in the Demeter package.

4. Electrochemical measurements

All electrochemical measurements were performed on a CHI 760E electrochemical workstation (Shanghai CHI Instruments Company) at 25 °C. The working electrode consisted of freshly prepared NF, Mn₃O₄, or Pt_{SA}-Mn₃O₄. The graphite carbon rod and saturated calomel electrode (SCE) served as the counter electrode and reference electrode, respectively. To prepare the Pt/C electrode, 1.90 mg of the commercial Pt/C and 5 μ L of 5 wt.% Nafion ethanol solution were dispersed in a mixture of 300 μ L of H₂O and 700 μ L of ethanol, and then this 1 mL mixture was loaded on NF. Electrochemical impedance spectroscopy measurements of the samples were recorded over a frequency range of 10⁶ Hz to 0.01 Hz. The SCE reference electrode was calibrated in the 1.0 M KOH electrolyte with the reversible hydrogen electrode (RHE) according to the formula E(RHE) = E(SCE) + 0.0591 pH + 0.241 V. All linear sweep voltammetry curves were treated by iR compensation.

5. The estimation of mass activity and turnover frequency (TOF)

(1) Pt mass activity calculation

To compare the Pt mass activities of Pt_{SA} -Mn₃O₄ and Pt/C, their activity values have been normalized to their Pt loadings, and the contributions of the MnO₂ and NF have been deducted. The details are as follows: As shown in Figure 4a, the HER activities for NF, Mn₃O₄, Pt_{SA}-Mn₃O₄ and Pt/C are 1.277, 3.317, 30.69 and 29.94 mA cm⁻², respectively, at the overpotential of 0.05 V.^[1] The Pt loading of Pt_{SA}-Mn₃O₄ was determined by ICP-OES to be 4.19 wt% and thus 0.073 mg cm⁻². The Pt loading of 20 wt% commercial Pt/C was 1.90 mg cm⁻². Because all the samples were supported by NF in the measurements, the Pt mass activities of Pt/C and Pt_{SA}-Mn₃O₄ can be calculated using the following equations to be 75 and 374 mA mg⁻¹, respectively.

$$j_{\text{Mass}}^{\text{Pt/C}} = \frac{j_{\text{Mass}}^{\text{Pt/C}} - j_{\text{Mass}}^{\text{NF}} (\text{mA cm}^{-2})}{\text{mass}_{\text{Pt}} (\text{mg cm}^{-2})} = \frac{29.94 - 1.277}{0.380} = 75 \text{ mA mg}^{-1}$$

$$j_{\text{mass}}^{\text{Pt}_{\text{SA}} - \text{Mn}_{3}\text{O}_{4}} = \frac{j_{\text{SA}}^{\text{Pt}_{\text{SA}} - \text{Mn}_{3}\text{O}_{4}} - j_{\text{mass}_{4}}^{\text{Mn}_{3}\text{O}_{4}} (\text{mA cm}^{-2})}{\text{mass}_{\text{Pt}}(\text{mg cm}^{-2})} = \frac{30.69 - 3.317}{0.073} 374.97 \text{ mA mg}^{-1}$$

(2) Calculation of TOF values

The TOF values were calculated according to previous reports.^[2] Take the calculation process of TOF value of Pt_{SA}-Mn₃O₄ as an example, the details are described as below:

 $TOF = \frac{Total hydrogen turnovers per geometric area}{Active sites per geometric area}$

The total number of hydrogen turnovers was calculated from the current density using the formula^[3]:

Total hydrogen turnovers

$$= \left[j \, (\text{mA cm}^{-2}) \right] \left[\frac{1 \, (\text{C s}^{-1})}{10^3 \, (\text{mA})} \right] \left[\frac{1 \, (\text{mol e}^{-})}{96485 \, (\text{C})} \right] \left[\frac{1 \, \text{mol H}_2}{2 \, \text{mol e}^{-1}} \right] \left[\frac{6.022 \times 10^{23} \, \text{molecules H}_2}{1 \, \text{mol H}_2} \right]$$

=
$$3.12 \times 10^{15} \,\mathrm{H_2 \, s^{-1} \, cm^{-2}}$$
 per mA cm⁻²

The number of active sites in Pt_{SA} - Mn_3O_4 catalyst was calculated from the total mass of Pt on the electrode and the atomic weight of Pt, if all Pt atoms contributed to the reaction process:

Accordingly, the active site density based on bulk Pt is:

$$= \left(\frac{0.073 \times 10^{-3} \text{ (g cm}^{-2}) \times 4.19 \text{ wt\%}}{195.078}\right) \left(\frac{6.022 \times 10^{23} \text{(Pt atoms)}}{1 \text{ (mol Pt)}}\right) = 9.44 \times 10^{15} \text{ Pt sites cm}^{-2}$$

Finally, the current density obtained from the LSV polarization curve are converted into TOF values according to:

TOF = $\frac{3.12 \times 10^{15}}{9.44 \times 10^{15}} \times |j| = 0.3305 \times |j| (s^{-1})$

6. Computational Methods and Models

First-principle calculations were performed by the density functional theory (DFT) using the Vienna Ab-initio Simulation Package (VASP) package.^[4] The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE) functional was used to describe the electronic exchange and correlation effects^[5]. Uniform G-centered k-points meshes with a resolution of 2π *0.04 Å⁻¹ and Methfessel-Paxton electronic smearing were adopted for the integration in the Brillouin zone for geometric optimization. The simulation was run with a cutoff energy of 500 eV throughout the computations. These settings ensure convergence of the total energies to within 1 meV per atom. Structure relaxation proceeded until all forces on atoms were less than 1 meV Å⁻¹ and the total stress tensor was within 0.01 GPa of the target value. To describe the on-site Coulomb interaction, the DFT +U approach was used to calculate all the elementary reaction steps, and the U term of Mn-3d is 4 eV.

The free energy of the adsorption atomic hydrogen (ΔG_{H^*}) is obtained by

 $\Delta G_{H^*} = \Delta E_{H^*} + \Delta E_{ZPE} - T\Delta S_{H^*}$

 ΔE_{H^*} describes the energy needed to increase the coverage by one hydrogen atom. $\Delta EZPE$ is the difference in zero point energy and ΔS_{H^*} is the difference in entropy. $\Delta E_{ZPE} - T\Delta S_{H^*}$ is about 0.24 eV, so $\Delta G_{H^*} = \Delta E_{H^*} + 0.24^{[6]}$.

For ΔE_{H^*} , it is calculated as follows:

 $\Delta E_{H^*} = E_{(surface+H)} - E_{surface} - 1/2 E_{(H2)}$

, where $E_{(surface+H)}$ represents the total energy of the selected surfaces with one adsorbed hydrogen atom on the surfaces, $E_{surface}$ represents the total energy of the surfaces, and $E_{(H2)}$ represents the total energy of a gas phase H_2 molecule.

Supplementary Figures



Figure S1. Characterization of Mn_3O_4 . (a) SEM image. (b) TEM image. (c) XRD pattern. (e) EDX spectrum.

For the measurement of XRD, the powder sample was scraped off the FTO conductive glass surface after electrodeposition.



Figure S2. Cyclic voltammetric curves of the Mn_3O_4 precursor sample after 500 potential cycles: (a) The curves were measured in 0.5 M Na₂SO₄ with a sweep rate of 100 mV s⁻¹ at room temperature; (b) Pt deposited on Mn_3O_4 : The curves were obtained in 0.5 M Na₂SO₄ containing 0.095 mM H₂PtCl₆•6H₂O with a sweep rate of 100 mV s⁻¹ at room temperature. (c) Curves obtained after 500 cycles of the glassy carbon electrode in 0.095 mM H₂PtCl₆•6H₂O at a scan rate of 100 mV s⁻¹.



Figure S3. (a) HER polarization curves and (b) Tafel plots of the samples after the cycles from 100 runs to 900 runs.



Figure S4. (a) Electrochemical Impedance Spectroscopy Nyquist plots of the Pt-Mn₃O₄-x. (b) Corresponding equivalent circuit diagram.

The EIS results of Pt-Mn₃O₄-3, Pt-Mn₃O₄-5, Pt-Mn₃O₄-7, and Pt-Mn₃O₄-9 in Figure S4 showed two semicircles. The first semicircle represents the charge transfer resistance at the electrode surface, while the second semicircle may be the resistance caused by uneven charge transfer within the system. The equivalent circuit used to simulate the EIS data takes into account a series resistance (R_s), two constant phase elements (CPE1 and CPE2), a resistance related to the charge transfer inhomogeneity in the system (R_p), and a charge transfer resistance related to the HER process (R_{ct}). The radius of the first semicircle became smaller with the increased Pt content. Due to the charge redistribution and faster charge transfer in the Pt bonded region, but slower charge transfer in the non-Pt bonded region.



Figure S5. SEM images of (a) Pt-Mn₃O₄-1, (b) Pt-Mn₃O₄-3, (c) Pt-Mn₃O₄-5, (d) Pt-Mn₃O₄-7, (e) Pt-Mn₃O₄-9.



Figure S6. (a, b) SEM images and (c, d) TEM images of Pt_{SA} -Mn₃O₄.



Figure S7. XRD patterns of Mn_3O_4 and Pt- Mn_3O_4 series catalysts. The typical (111) and (200) peaks of crystalline Pt at ca. 40° and 47° are absent.



Figure S8. Cyclic voltammograms (CVs) of Pt-Mn₃O₄ series catalysts, PtNF series catalysts, and Mn₃O₄. CV measurements were taken in N₂-saturated (a,b) 1.0 M KOH and (c,d) 1.0 M PBS with a scan rate of 50 mV s⁻¹.

As a comparison, the CV curves of direct Pt growth by NF at the different number of scan segments are given.



Figure S9. (a) The polarization curves for mass activity of samples. (b) Mass activity of Pt- Mn_3O_4 -1, Pt- Mn_3O_4 -3, Pt- Mn_3O_4 -5, Pt- Mn_3O_4 -7, and Pt- Mn_3O_4 -9 at an overpotential of 0.05 V.



Figure S10. STEM-EDX spectrum of the Pt_{SA} -Mn₃O₄.



Figure S11. Pt 4f XPS spectrum of Pt/C and Pt_{SA}-Mn₃O₄.



Figure S12. (a) Pt 4f XPS spectra and (b) XPS survey of Pt/C and Pt-Mn₃O₄ series catalysts.

As shown in Figure S12a, the Pt 4f peaks of the catalysts shifted toward higher binding energies with increasing Pt content, which was due to the progressively enhancing EMSI effect in the samples. The full XPS spectrum in Figure S12b shows that the intensity of Pt signal peaks in Pt-Mn₃O₄-1, Pt-Mn₃O₄-3, Pt-Mn₃O₄-5, Pt-Mn₃O₄-7, and Pt-Mn₃O₄-9 are weak with Pt/C, revealing the low content of Pt.



Figure S13. XPS spectra of Mn_3O_4 and Pt_{SA} - Mn_3O_4 .



Figure S14. High-resolution Mn 2p XPS spectra of the Mn₃O₄, V_{Mn}-Mn₃O₄ and Pt_{SA}-Mn₃O₄.

Here V_{Mn} -Mn₃O₄ is the sample obtained after 500 potential cycles of Mn₃O₄ in 0.5 M Na₂SO₄ without H₂PtCl₆•6H₂O.



Figure S15. ESR spectra of Mn_3O_4 , V_{Mn} - Mn_3O_4 and Pt_{SA} - Mn_3O_4 .



Figure S16. (a) Raman spectra of the Mn_3O_4 and Pt- Mn_3O_4 series catalysts. (b) Schematic diagram of the change in bond length of tetrahedral Mn-O bonds during the formation of vacancies by Mn dissolution and Pt embedding.



Figure S17. The DFT-optimized structure for (a, a') Mn₃O₄, (b, b') Pt doping into tetrahedral sites, and (c, c') Pt doping into the octahedral site. (a-c:Top view. a'-c':Side view, Red: O; Blue: Mn; Grey: Pt).



Figure S18. Side view of the charge density difference distribution for (a) Mn_3O_4 and (b) Pt_{SA} - Mn_3O_4 . (Red: O; Blue: Mn; Grey: Pt). The yellow and blue isosurfaces represent electron accumulation and donation, respectively. Pt atoms occupy the Octahedral sites.



Figure S19. Calculated partial density of states (PDOSs) of Mn_3O_4 and $Pt_{SA}-Mn_3O_4$. PDOSs above zero represent spin-up states, and those below zero represent spin-down states. The vertical dotted line represents the Fermi energy level (E_F set to zero).



Figure S20. Illustrative example of alkaline HER mechanism on Pt_{SA} -Mn₃O₄. The catalytic cycle is initiated by adsorption of H₂O onto Mn (step I), the absorbed H₂O is then dissociated into absorbed H (H*) on Pt and OH*(step II), followed by another proton from an adjacent H₂O molecule reacting with the first H* to generate H₂ (steps III–V). (Red: O; Blue: Mn; Grey: Pt; green: H).



Figure S21. Double-layer capacitance analyses. CV curves of (a) Mn₃O₄ and (b) Pt_{SA}-Mn₃O₄.



Figure S22. The plots of current densities against scan rates. ($\Delta j = (j_a - j_c)/2$, j_a and j_c represent the anodic and cathodic current densities at a same potential, respectively).



Figure S23. (a) SEM images and (b) TEM images of Pt_{SA} -Mn₃O₄ after long-time operation.



Figure S24. Elemental mapping of Pt_{SA} -Mn₃O₄ after the stability test.



Figure S25. characterizations of Pt_{SA} -Mn₃O₄ after long-time operation (a) XRD pattern. (b) Pt 4f XPS spectrum.

Supplementary Tables

Table S1. The Pt loading amount in Pt- Mn_3O_4 -1, Pt- Mn_3O_4 -3, Pt- Mn_3O_4 -5, Pt- Mn_3O_4 -7, and Pt- Mn_3O_4 -9 obtained from the ICP-OES results.

catalysts	Pt loading amount (mg cm ⁻²)	Mass percentage (%)	
Pt-Mn ₃ O ₄ -1	0.027	1.58	
Pt-Mn ₃ O ₄ -3	0.034	2.00	
Pt-Mn ₃ O ₄ -5	0.073	4.19	
Pt-Mn ₃ O ₄ -7	0.277	13.93	
Pt-Mn ₃ O ₄ -9	0.225	11.84	

samples	Shell	CN	R (Å)	σ^2	R-factor
	Pt-O	4.27	2.15	0.011	
Pt _{SA} -Mn ₃ O ₄	Pt-O	2.27	2.56	0.001	0.0088
	Pt-Mn	2.49	2.87	0.008	
Pt foil	Pt-Pt	12(fixed)	2.766	0.0046	0.0017
PtO ₂	Pt-O	6(fixed)	2.016	0.0028	

Table S2. FT-EXAFS fitting results of Pt_{SA} -Mn₃O₄, Pt foil, and PtO_2 was given as a reference.

CN: coordination numbers of identical atoms; R: interatomic distance; σ^2 : Debye-Waller factors; ΔE_0 : energy shift. R factor: goodness of fit. S_0^2 was set to 0.818, according to the experimental EXAFS fit of Pt foil reference by fixing CN as the known crystallographic value.

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Electrocatalysts	Electrolyte	η@10 mA cm ⁻²	Tafel slope	Reference	
Pt _{SA} -Mn ₃ O ₄	1 M KOH	24	54	This work	
Pt ₁ /N-C	1 M KOH	46	36.8	Nat. Commun. 2020, 11, 1029	
Pt/np-Co _{0.85} Se	1 M KOH	58	39	Nat. Commun. 2019, 10, 1743	
PtSA-NT-NF	1 M KOH	20	-	Angew. Chem. Int. Ed. 2017 , 56, 13694- 13698	
er-WS ₂ -Pt	1 M KOH	~48	65	Adv. Mater. 2018, 30, 1704779	
Pt@PCM	1 M KOH	139	73.6	Sci. Adv., 4, eaao6657	
Pt-SAs/MoSe ₂	1 M KOH	29	34	Nat. Commun. 2021, 12, 3021	
Pt-SAs/MoS ₂	1 M KOH	65	50		
$Pt_{SA}-C_1N_1$	1 M KOH	46	36.8	Nat. Commun. 2020, 11, 1029	
Pt _{SA} -Co(OH) ₂	1 M KOH	29	35	Energy Environ. Sci. 2020 , 13, 3082- 3092	
Pt ₁ @Fe-N-C	1 M KOH	108	/	Adv. Energy Mater. 2018, 8, 1701345	
Ru-MoS ₂ /CC	1 M KOH	41	114	<i>Appl. Catal. B- Environ.</i> 2019 , <i>249</i> , 91- 97	
Pt _{sa} -NiO/Ni	1 M KOH	26	27	Nat. Commun. 2021, 12, 3783	
IrCo@N-C	1 M KOH	45	80	Adv. Mater. 2018, 30, 1705324	
RuCo@N-C	1 M KOH	28	31	Nat. Commun. 2017, 8, 14969	
Ru-MoO ₂	1 M KOH	29	44	J. Mater. Chem. A 2017, 5, 5475-5485	
Ru/g-C ₃ N ₄ -C- TiO ₂	1 M KOH	107	85	ACS Appl. Mater. Interfaces 2021 , 13, 46608-46619	
Pt/TiB _x O _y	1 M KOH	~200	135	ACS Catal. 2022, 12, 5970-5978	
1.1 wt% Pt/MoO ₂	1 M KOH	14	35.76	Chem. Eng. J. 2022, 427, 131309	
Pt-SL/TiO ₂	1 M KOH	210	79	Small 2021, 17, 2100732	
Pt/TiB _x O _y	1 M KOH	~200	135	ACS Catal. 2022, 12, 5970-5978	
1.1 wt% Pt/MoO ₂	1 M KOH	14	35.76	Chem. Eng. J. 2022 , 427, 131309	
Pt-SA/TiO ₂	1 M KOH	-	410		

Table S3. HER performances of this work and other reported electrocatalysts in alkaline media.

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