Electronic Supplementary Material (ESI) for Nanoscale Advances.

Supporting Information

Introduction of Mn(III) to regulate the electronic structure of F-doped nickel hydroxide for efficient water oxidation

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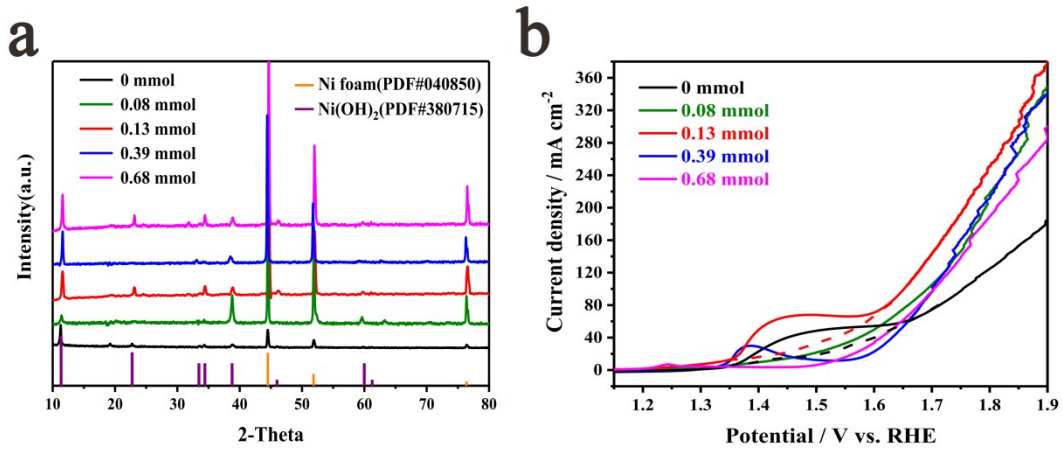

Fig. S1. (a) XRD comparison of different doping amounts of Mn in Mn-F/$Ni(OH)_2$-NF (b) LSV of different Mn doping amounts.

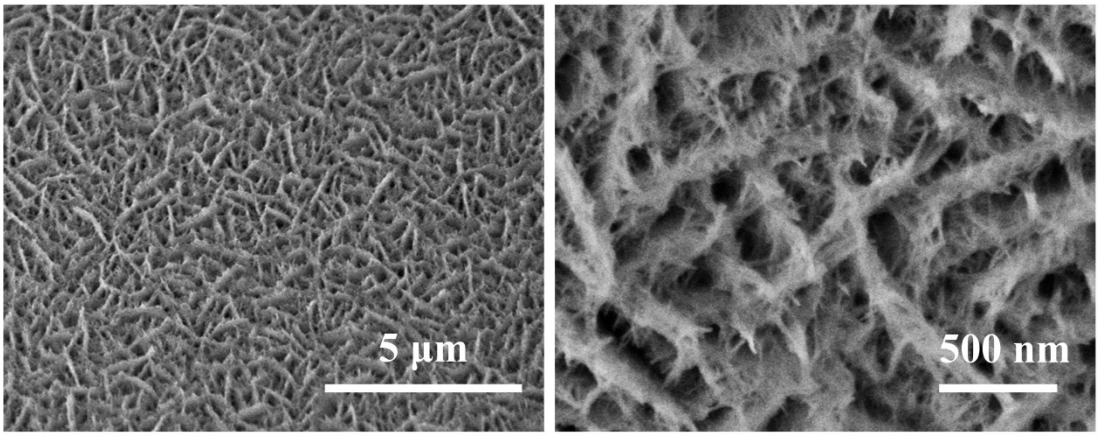

Fig. S2. SEM images of Mn-F/$Ni(OH)_2$-NF.

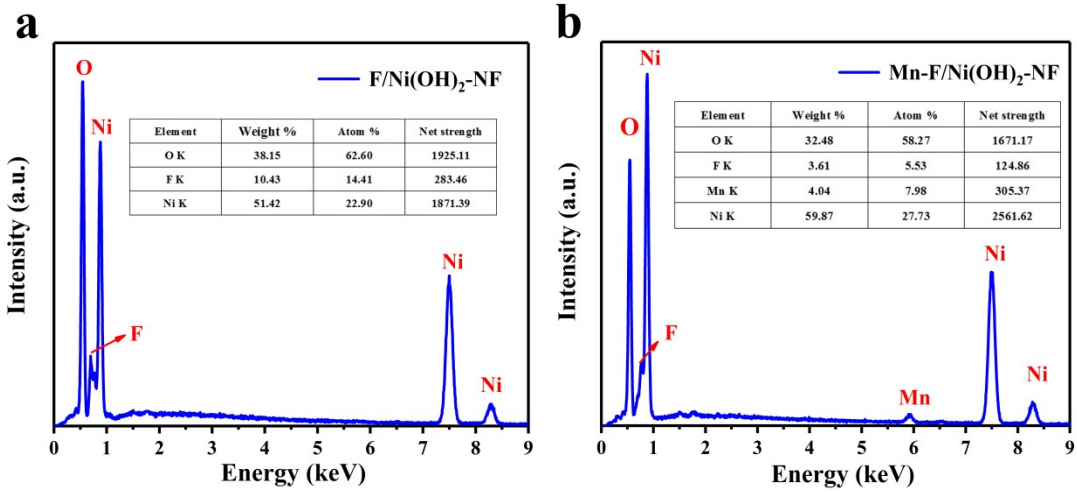

Fig. S3. EDX spectrum of (a) F/Ni(OH)$_2$-NF and (b) Mn-F/Ni(OH)$_2$-NF.

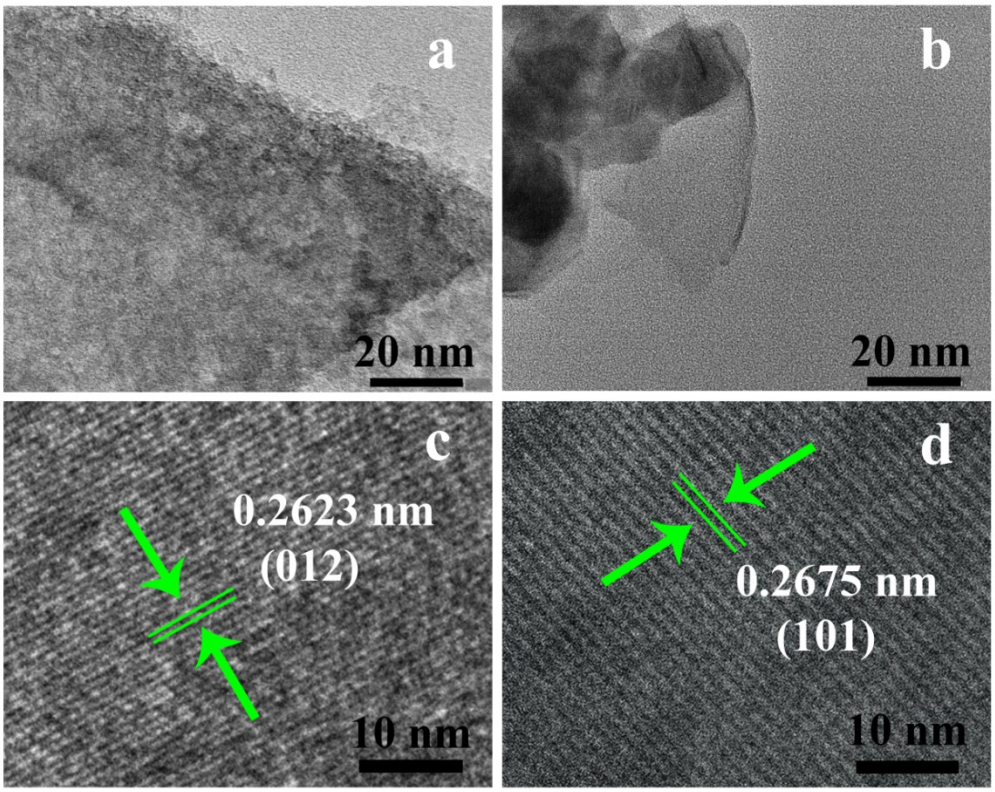

Fig. S4. (a) TEM of F/Ni(OH)$_2$-NF. (b) TEM of Mn-F/Ni(OH)$_2$-NF. (c) HRTEM of F/Ni(OH)$_2$-NF (d) HRTEM of Mn-F/Ni(OH)$_2$-NF.

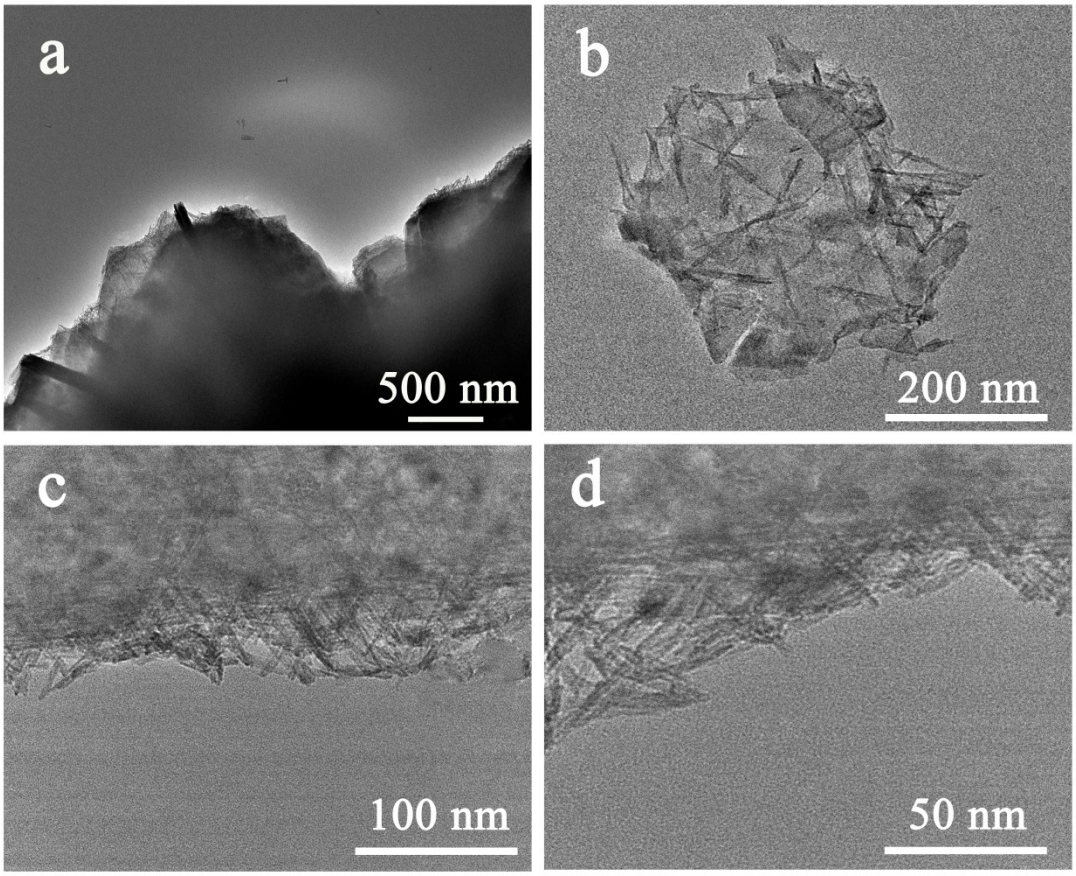

Fig. S5. TEM of Mn-F/$Ni(OH)_2$-NF.

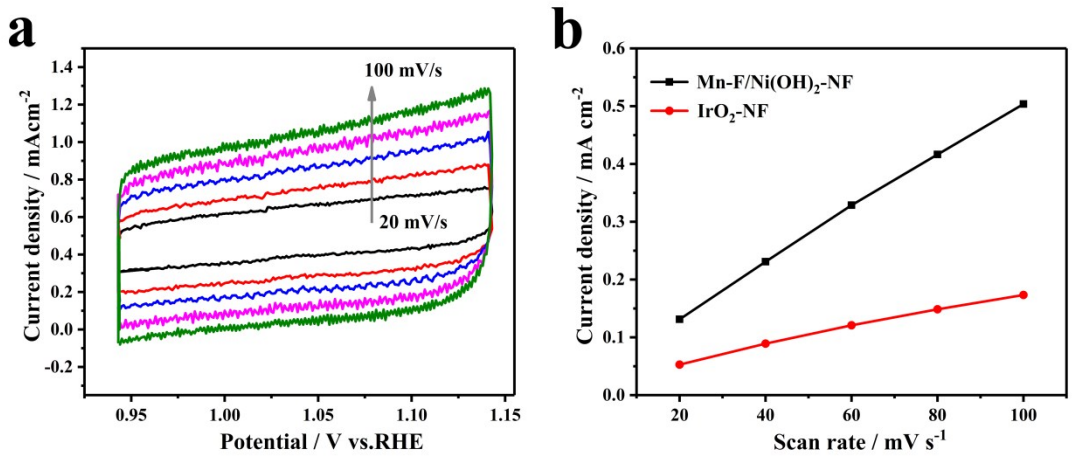

Fig. S6. (a) Electrochemical cyclic voltammetry curves of Mn-F/$Ni(OH)_2$-NF at different sweep speeds (voltage range 0.94 - 1.14 V *vs.* RHE) (b) Electric double layer capacitance curves of Mn-F/$Ni(OH)_2$-NF and IrO_2-NF.

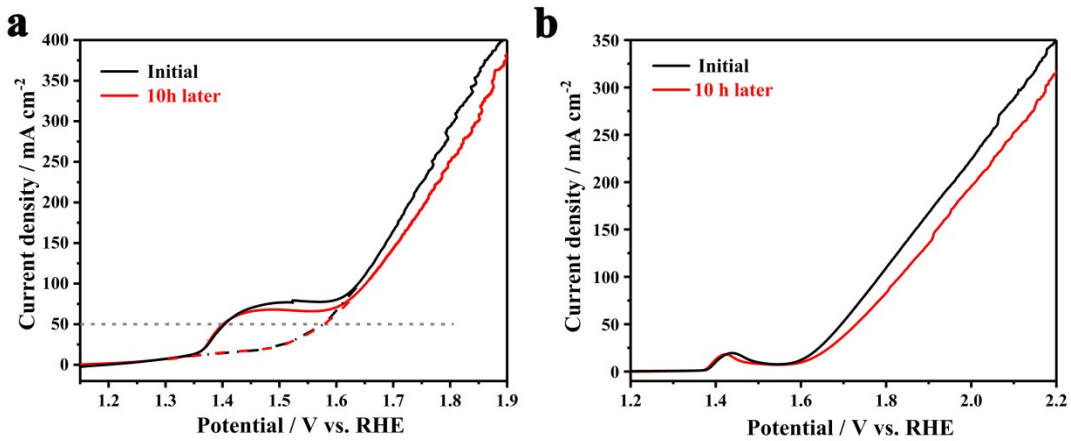

Fig. S7. LSV comparison of (a) Mn-F/$Ni(OH)_2$-NF and (b) IrO_2-NF before and after 10 hours' stability test. The dotted line in the figure is the OER evolution curve in the range of 1.35-1.65 V *vs*. RHE.

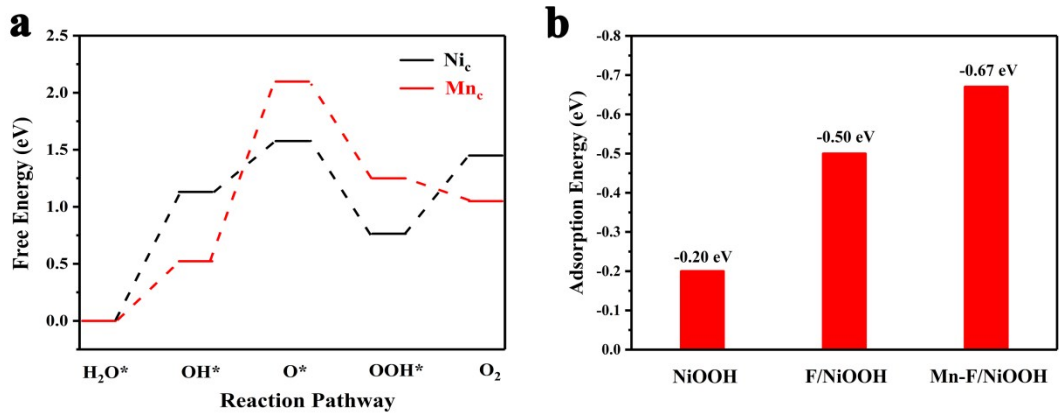

Fig. S8. (a) The standard free energy diagram of the OER process with Ni and Mn as active centers in the Mn-F/NiOOH material. (b) The adsorption energy of H_2O on the NiOOH, F/NiOOH and Mn-F/NiOOH.

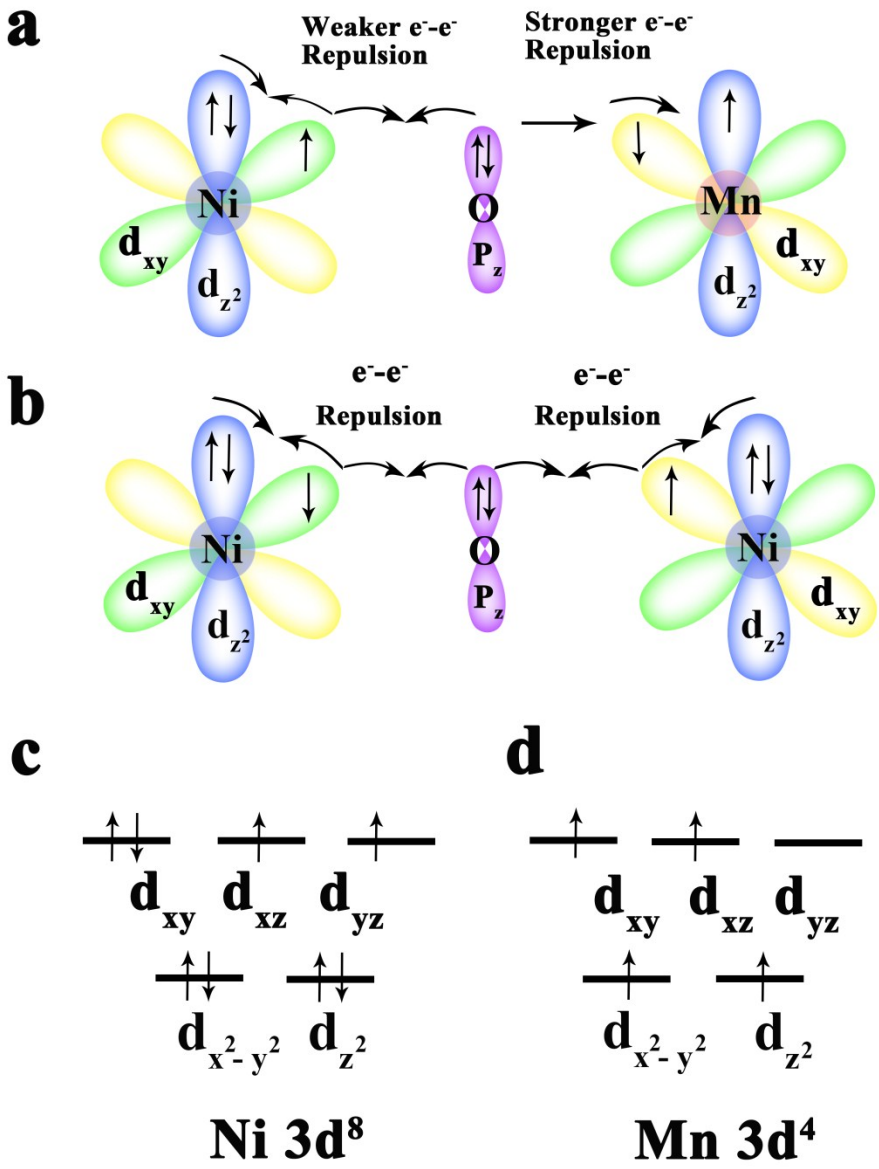

Fig. S9. (a) Schematic diagram of electronic coupling process between Ni and Mn. (b) Schematic diagram of electronic coupling process between Ni and Ni. (c,d) Electron splitting of Ni and Mn 3d orbitals in the crystal fields.

Computational details

Our density functional theory (DFT) calculations was performed by applying the QuantumATK software package [1]. The local density approximation (LDA) with the Perdew-Zunger parametrization [2] of the correlation energy was adopted as the exchange correlation potential. The interaction between cores and valence electrons

for all atoms is modeled with Troullier-Martins nonlocal pseudopotential, and double-zeta plus polarized (DZP) basis sets are employed.

The OER reaction process can be represented as follows in an alkaline electrolyte solution:

$$OH^- + * \rightarrow OH^* + e^- \quad (1)$$

$$OH^* + OH^- \rightarrow O^* + H_2O + e^- \quad (2)$$

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

$$OOH^* + OH^- \rightarrow O_2 + H_2O + e^- \quad (4)$$

where * presents the adsorption site on the surface of catalysts, OH*, O*, and OOH* represents the intermediate of the reaction.

In order to simplify the calculation process, the basic steps (1)-(4) are converted to the form of acidic conditions as follows

$$2H_2O + * \rightarrow OH^* + H_2O + e^- + H^+ \quad (5)$$

$$OH^* + H_2O \rightarrow O^* + H_2O + e^- + H^+ \quad (6)$$

$$O^* + H_2O \rightarrow OOH^* + e^- + H^+ \quad (7)$$

$$OOH^* \rightarrow O_2 + e^- + H^+ \quad (8)$$

The steps (1)-(4) are equivalent to (5)-(8).

At standard conditions, the Gibbs free energy changes for reaction (5)-(8) are calculated as:

$$\Delta G_1 = \Delta G_{OH^*} - eU + kT\ln 10 pH \quad (9)$$

$$\Delta G_2 = \Delta G_{O^*} - \Delta G_{OH^*} - eU + kT\ln 10 pH \quad (10)$$

$$\Delta G_3 = \Delta G_{OOH^*} - \Delta G_{O^*} - eU + kT\ln 10 pH \quad (11)$$

$$\Delta G_4 = 4.92\ eV - \Delta G_{OOH^*} - eU + kT\ln 10 pH \quad (12)$$

The theoretical overpotential is defined as:

$$\eta_{Theory} = \max[\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4]/e - 1.23\ V.$$

G represents the Gibbs free energy, and U represents external bias against normal hydrogen electrode (NHE) at standard conditions (T = 298.15 K, P = 1 bar, pH = 0). So, eU and pH are 0. According to the calculation of Gibbs free-energy, the

theoretical overpotential of NiOOH, F/NiOOH and Mn-F/NiOOH is 1.90, 0.47, and 0.35 eV, respectively.

Table. S1. Calculated Gibbs free energies (eV) of OER elementary steps and overpotential under reaction condition (pH = 14) on NiOOH, F/NiOOH and Mn-F/NiOOH.

Materials	ΔG_1	ΔG_2	ΔG_3	ΔG_4	Overpotential(eV)
NiOOH	1.28	3.13	0.35	0.16	1.90
F/NiOOH	1.21	1.70	0.93	1.08	0.47
Mn-F/NiOOH	1.13	1.58	0.76	1.45	0.35

References

[1] QuantumATK version 2018.06, Synopsys QuantumATK.

[2] J. P. Perdew and A. Zunger, *Phys. Rev. B*, 1981, **23**, 5048.

[3] M. Y. Li, L. F. Chen, S. T. Ye, G. L. Fan, X. Zhang and F. Li, *J. Mater. Chem. A*, 2019, **7**, 3695-13704.