## Supporting Information

## Activating Basal Plane in NiFe Layered Double Hydroxide by Mn<sup>2+</sup> doping for Efficient and Durable Oxygen Evolution Reaction

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Chemicals and instruments: Chemicals including NiCl<sub>2</sub>•6H<sub>2</sub>O, FeCl<sub>2</sub>•9H<sub>2</sub>O, FeSO<sub>4</sub>, MnCl<sub>2</sub>, and ZnCl<sub>2</sub> were purchased from Sinopharm Chemical Reagent Co, Ltd. (SCRC). Urea and KOH were purchased from Beijing Chemical Reagents Company. Deionized water with a resistivity  $\geq 18$  M $\Omega$  was used to prepare all aqueous solutions. All the reagents were of analytical grade and were used without further purification.

The morphologies of as-prepared samples were characterized by transmission electron microscopy (TEM; FEI Tecnai G<sup>2</sup> 20) and scanning electron microscopy (SEM; Zeiss SUPRA 55). X-ray diffraction (XRD) patterns were collected on Shimadzu XRD-6000 with Cu K $\alpha$  radiation (40 kV, 30 mA,  $\lambda$  = 1.5418Å), recorded with 2 $\theta$  ranging from 5° to 70°. X-ray photoelectron spectroscopy (XPS) measurements were carried out with a PHI Quantera II XPS Scanning Microprobe.

Synthesis of pristine and doped NiFe-LDHs array: NiFe-LDH on Nickel foam (NiFe-LDH array) was synthesized by hydrothermal method. In a typical procedure, NiCl<sub>2</sub>•6H<sub>2</sub>O (0.66 mmol), FeCl<sub>2</sub>•9H<sub>2</sub>O (0.33 mmol) and CO(NH<sub>2</sub>)<sub>2</sub> (10 mmol) were dissolved in 36 mL of distilled water and stirred to form a clear solution. Nickel foam (about 3 cm  $\times$  2 cm) was carefully cleaned with concentrated HCl solution (37 wt%) in

an ultrasound bath for 5 min in order to remove the surface nickel oxide layer, and then washed by deionized water and absolute ethanol respectively for 5 min to remove the residual acid. The solution and the Nickel foam were transferred to a 40 mL Teflonlined stainless-steel autoclave, which was sealed, maintained at 120 °C for 12 h, and then allowed to cool to room temperature naturally. A brown metal substrate was formed and subsequently rinsed with distilled water, ethanol each for 5 minutes with the assistance of ultrasonication. The prepared NiFe-LDH array was dried by air blower in cold air for 5 min. By using 0.10 mmol MnCl<sub>2</sub> precursor to replace 0.10 mmol NiCl<sub>2</sub>•6H<sub>2</sub>O, the Mn<sup>2+</sup>-doped NiFe-LDH array was prepared. Distilled water was bubbled by  $N_2$  for 30 min to get rid of dissolved oxygen. The residual air in the autoclave was also replaced by  $N_2$  to the greatest extent to keep the  $Mn^{2+}$  from oxidation by oxygen prior to hydrothermal process. And the teflon-lined stainless-steel autoclave was sealed and maintained at 120 °C for 12 h in vacuum oven. For comparison, Mn4+doped NiFe-LDH from Mn<sup>4+</sup> precursor was also prepared under O<sub>2</sub> bubbling environment. Mn<sup>2+</sup> was pre-oxidized to Mn<sup>4+</sup> until no color can be observed prior to hydrothermal process, and the Mn4+-doped NiFe-LDH array was obtained after maintaining at 120 °C for 12 h.

*Electrochemical measurements:* The electrocatalytic water oxidation of the asprepared materials were studied with a three-electrode system in 1.0 M aqueous KOH solution using a CHI 660D workstation. A saturated calomel electrode (SCE) and a platinum plate were used as the reference and the counter electrode, respectively. To prepare working electrode, 1 cm  $\times$  1 cm NiFe-LDH array or Mn<sup>2+</sup>-doped NiFe-LDH was prepared. After twenty cyclic voltammetric scans, the polarization data were collected using linear sweep voltammetry at a scan rate of 1 mV/s. The electrochemical impedance spectroscopy measurements were carried out in the same configuration at open circuit voltage from 10<sup>5</sup>-0.1 Hz. The stability of the electrode was first measured by testing the CV at 5 mV/s for 750 cycles (potential range 1.0 V to 2.0 V vs. RHE), and then the i-t curve stability test of Mn<sup>2+</sup>-doped NiFe-LDH was conducted at current density of 50 mA/cm<sup>2</sup> for 40 h. The values of TOF were calculated by assuming that all metal atoms are involved in the catalytic processes:

 $TOF = J \times s/4 \times F \times n$ 

where J (mA/cm<sup>2</sup>) is the current density at a measured potential, s represents the surface area of the electrode, F is the Faraday's constant (96485.3 C mol<sup>-1</sup>), and n is the amount of active sites in NiFe-LDH array estimated by ECSA (potential range 0-0.15 V, scan rate 1 mV/s -5 mV/s).

## Laviron equation

 $E_c = E_{1/2} - (RT/\alpha nF) \times \ln (\alpha nF/RTk_s) - (RT/\alpha nF) \times \ln (v)$ , where Ec is the reduction potential of metal redox,  $E_{1/2}$  is the formal potential of metal redox, R is the universal gas constant, T is the temperature in kelvin, n is the number of electrons transferred,  $\alpha$ is the transfer coefficient, ks is the rate constant of metal redox, and v is the scan rate in the CV measurements.

*Computational details:* DFT + U calculations were employed to analyze the role of Mn doping in the NiFe LDH structure during the water oxidation progress. The (110)

surface was taken into consideration as the surface corresponds to the edge of LDH structure mostly. To simulate the Mn<sup>2+</sup>-doped NiFe-LDH, the Ni atoms were replaced by Mn atoms. For pristine and Mn<sup>2+</sup>-doped NiFe-LDH (110) facets, Fe atoms were used as the active sites for water oxidation.

All calculations were performed using the projector-augmented wave method and a plane-wave basis set as implemented in the Vienna Ab Initio Simulation Package (VASP). The bulk and surface properties of NiFe-LDHs were optimized within GGA-PBE. A full optimization of all atom positions in the bulk was performed via the action of a conjugate gradient optimization procedure. The bulk lattice constants were optimized using the  $5\times5\times5$  Monkhorst-Pack k-point sampling. The cutoff energy for plane-wave basis functions was set to 450 eV with the energy change convergence criterion of  $1\times10^{-4}$  eV. Atomic positions were allowed to relax until the sum of the absolute forces is less than 0.05 eV/Å. Hubbard-U Correction method (DFT+U) was applied to improve the description of localized Ni and Fe d-electrons in the NiFe-LDHs with U=5.30, U=3.90 and U=6.45 for Fe, Mn and Ni, respectively. Spin polarization was considered in all the calculations. The electron density evolution of different metal sites was studied by Bader charge.



**Figure S1** XPS of Ni (A) and Fe (B) in pristine NiFe-LDH and Mn<sup>4+</sup>-doped NiFe-LDH from oxidized precursor as a control sample. The binding energy of Ni, Fe sites in NiFe-LDH shows negligible change before and after Mn doping using Mn<sup>4+</sup> precursor.



Figure S2 EIS of pristine NiFe-LDH and Mn<sup>4+</sup>-doped NiFe-LDH as a control sample.



**Figure S3** Total density of states (TDOS) diagram of pristine NiFe-LDHs and Mn<sup>2+</sup>doped NiFe-LDHs. The narrower bandgap of Mn<sup>2+</sup>-doped NiFe LDHs indicates a more conductive structure compared to the pristine NiFe-LDHs.



**Figure S4** Electrochemical surface area (ECSA) of A: pristine NiFe-LDH and B: Mn<sup>2+</sup>-doped NiFe-LDH. Potential range: 0-0.15 V. Scan rate range: 1mV/s to 5 mV/s.



Figure S5 ECSA normalized LSV of pristine and Mn<sup>2+</sup>-doped NiFe-LDH



**Figure S6** CV curves of different electro-catalysts before and after 750 cycles between 1.0 V to 2.0 V (vs. RHE) with scan rate of 5 mV/s.



Figure S7 XPS of Fe (A), Ni (B) and Mn (C) in Mn-doped NiFe-LDH before and after water oxidation test



Figure S8 Laviron analysis of pristine NiFe-LDH based on different scan rates.



**Figure S9** XRD of Fe<sup>2+</sup>or Zn<sup>2+</sup>-doped NiFe-LDH, respectively, in comparison with pristine NiFe-LDH



Figure S10 SEM of  $Fe^{2+}$  and  $Zn^{2+}$  doped NiFe-LDH, respectively. The scale bar represents 500 nm.



**Figure S11** Electronic structure of Ni and Fe sites in Fe<sup>2+</sup> or Zn<sup>2+</sup> doped NiFe-LDH, in comparison with pristine NiFe-LDH.



Figure S12 LSV of Fe<sup>2+</sup> or Zn<sup>2+</sup>-doped NiFe-LDH in comparison with pristine NiFe-LDH



Figure S13 LSV of colloid NiFe-LDH and Mn<sup>2+</sup>-doped NiFe-LDH

Catalyst	Electrolyte	Substrate	Onset potential	Overpotential	Ref.
			(V)	at 10 mA/cm <sup>2</sup>	
				(mV)	
<sup>S</sup> Au/NiFe-LDH	1 M KOH	/		237	[1]
NiFe-LDH	1 M KOH	/		263	[1]
Fe <sub>0.33</sub> Co <sub>0.67</sub> OOH	1 M KOH	Ni foam		266	[2]
PNSAs/CFC					
NiFeV-LDHs/NF	1 M KOH	Ni foam		231	[3]
UF NIFe-LDH	1 M KOH	/		254	[4]
Cu@NiFe LDH	1 M KOH	Cu foam		199	[5]
NiFeCr-LDH	1 M KOH	Carbon		280	[6]
		paper			
Co-UNMs	1 M KOH	/	1.49	307	[7]
FeCoP UNSAs	1 M KOH	Ni foam	1.48		[8]
NiFe-MOF	0.1 M KOH	Ni foam		240	[9]
NiFe-UMNs	1 M KOH	/	1.45	260	[10]
Ceria/Ni-TMO	1 M KOH	Ni foam		210	[11]
Co <sub>5</sub> Mo <sub>1.0</sub> O	1 M KOH	Ni foam		270	[12]
NSs@NF					
h-NiFeCr/NF	1 M KOH	Ni foam	1.43	200	[13]
NiFeS/NF	1 M KOH	Ni foam		230	[14]
CoFeOx	1 M KOH	Au	1.52	320	[15]
CoVOx	1 M KOH	/	1.53	351	[16]
O-Co3O4	1 M KOH	Ni foam	1.45	230	[17]
<b>Mn-doped</b>	1 M KOH	Ni foam	1.41	190	This work
NiFe-LDH					

Table S1 Activity comparison of state of the art OER electro-catalysts in alkaline electrolyte.

Table S2 Turnover frequency (TOF) of pristine and Mn<sup>4+</sup>-doped NiFe-LDH at

overpotential of 300 mV							
TOF $(s^{-1})$	Pristine NiFe-	Mn <sup>2+</sup> -doped	Mn <sup>4+</sup> -doped	Fe <sup>2+</sup> -doped	Zn <sup>2+</sup> -doped		
	LDH						
	0.11	0.30	0.14	0.24	0.08		

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