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## Supporting Information

# Single Atoms (Pt, Ir and Rh) Anchored on Activated NiCo LDH for Alkaline Hydrogen Evolution Reaction

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#### 1. Experimental Section

#### **1.1 Material preparation**

#### Synthesis of NiCo LDH and A-NiCo LDH

The NiCo LDH was prepared by an electrochemical deposition approach. The electrolyte was containing 10 mM Ni(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$  and 20 mM Co(NO<sub>3</sub>)<sub>2</sub>· $6H_2O$ . And a constant potential electrodeposition process was conducted at -1 V vs. SCE for 20min on a IVIUM electrochemical working station. After that, the NiCo LDH was activated by CV scan for 25 cycles with the scan rating of 20mV s<sup>-1</sup> in the potential range of -0.9~-1.6V vs. RHE, generating A-NiCo LDH.

#### Synthesis of M/A-NiCo LDH (M=Pt, Ir and Rh)

Electrochemical deposition of metal (*Pt, Ir and Rh*) on A-NiCo LDH supports were conducted using the linear sweep voltammetry method. 1M KOH solution containing 0.4mM metal precursors (IrCl<sub>3</sub>:xH<sub>2</sub>O, H<sub>2</sub>PtCl<sub>6</sub> and Na<sub>2</sub>RhCl<sub>6</sub>) was used as the electrolyte. The electrodeposition process was carried out from 0.1V to -0.4V vs. RHE with a sweeping rate of 5 mVs<sup>-1</sup>. The processes were repeated for ten times. In comparison, the NiCo LDH as working electrode for the M (Pt, Ir, Rh)/NiCo LDH was also fabricated via the same procedure as the mentioned above.

## 1.2 Structural characterization

Powder XRD pattern were characterized by a Bruker/D8 Advanced with Cu K $\alpha$  radiation ( $\lambda$ =0.15418 nm). Scanning electron microscopy (SEM) images were performed on a Hitachi S4800. Transmission electron microscopy (TEM) and high-angle annular dark-field transmission electron microscopy (HAADF-STEM) images were recorded on JEOL JEM-2100F and JEM-ARM200F, respectively. X-ray photoelectron spectra (XPS) data were tested by Thermo Scientific ESCALAB 250Xi to evidence the chemical states of samples. Raman measurement was performed with InVia reflex Raman spectrometer from Renishaw.

#### **1.3 Electrochemical measurements**

The electrochemical measurements were performed on a three-electrode cell by CHI 660e working station. The as synthesized LDH based materials was directly used as the working electrode, the graphite rod and standard calomel electrode (SCE) were employed as the counter electrode and reference electrode, respectively. The potential was converted to RHE by the

equation:  $E_{RHE}=E_{SCE}+0.059PH+0.242$  V. The geometric surface area of LDH based working electrode is 1 cm<sup>2</sup>. In comparison, 20wt% Pt/C ink was also coated onto carbon cloth with the mass loading of 1 mg cm<sup>-2</sup> for electrochemical tests. The HER polarization curves were measured by LSV method at a sweep rating of 5 mV s<sup>-1</sup> in 1M KOH electrolyte with a 95% IR compensation. EIS measurements were carried out with frequency ranging from 100 KHz to 0.1 Hz.

### **1.4 DFT theoretical calculation**

All the calculations were performed within the framework of the density functional theory (DFT) as implemented in the Vienna Ab initio Software Package (VASP 5.4.4) code within the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation and the projected augmented wave (PAW) method<sup>1-3</sup>. The cutoff energy for the plane-wave basis set was set to 400 eV. The Brillouin zone of the surface unit cell was sampled by Monkhorst-Pack (MP) grids<sup>4</sup>. The Pt, Ir, and Rh-doped NiFe LDH surfaces were determined by  $3 \times 3 \times 1$  Monkhorst–Pack grid. The convergence criterion for the electronic self-consistent iteration and force was set to 10-5 eV and 0.01 eV/Å, respectively. A vacuum layer of 15 Å was introduced to avoid interactions between periodic images. The PBE+U approach was applied to calculations of the electronic structure of NiFe LDH which can partly reduce the underestimation of the electronic band gap and the excessive tendency to delocalize the electron density. In this work, we set the Hubbard parameter to U-J = 6 and 4 for Ni and Fe, which ensures a good qualitative description of structure and electronic properties of NiFe LDH.

## 2. Additional Figures



Fig. S1. XRD patterns of NiCo LDH, Ir/A-NiCo LDH, Pt/A-NiCo LDH and Rh/A-

NiCo LDH samples.



Fig. S2. (a, b) SEM images, (b) TEM image and (d) EDS mapping images of NiCo LDH



Fig. S3. (a, b) SEM images, (b, c) TEM image and (d) elemental mapping images of A-NiCo LDH.



Fig. S4. (a, b) SEM images, (c, d) TEM images image of Ir/A-NiCoLDH.



Fig. S5. (a, b) SEM images, (c) HAADF-STEM image and (d) elemental mapping of TEM image of Rh/A-NiCo LDH.



Fig. S6. Elemental mapping of aberration-corrected TEM image for Rh/A-NiCo LDH.



Fig. S7. Elemental mapping of aberration-corrected TEM image for Pt/A-NiCo LDH.



Fig. S8. Elemental mapping of TEM image for Ir/A-NiCo LDH.



Fig. S9. EDS spectrum of Pt/A-NiCo LDH.



Fig. S10. EDS spectrum of Ir/A-NiCo LDH.



Fig. S11. EDS spectrum of Rh/A-NiCo LDH.



Fig. S12. EDS spectra of Pt/NiCo LDH, Ir/NiCo LDH and Rh/NiCo LDH samples.



Fig. S13. (a) XPS survey spectra of NiCo LDH, A-NiCo LDH, Pt/A-NiCo LDH, Ir/A-NiCo LDH and Rh/A-NiCo LDH.



Fig. S14 XPS spectra of (a) Ir/A-NiCo LDH and (b) Rh/A-NiCo LDH.



Fig. S15. LSV curves of Pt/A-NiCo LDH and Pt/NiCo LDH catalysts.



Fig. S16. LSV curves of Ir/A-NiCo LDH and Ir/NiCo LDH catalysts.



Fig. S17. LSV curves of Rh/A-NiCo LDH and Rh/NiCo LDH catalysts.



Fig. S18. Comparison of HER overpotentials at  $\eta_{10}$  for noble metal single atoms based electrocatalysts.



**Fig. S19.** Cyclic voltammograms of (a) NiCo LDH, (b) Pt/A-NiCo LDH, (c) Ir/A-NiCo LDH, (d) Rh/A-NiCo LDH electrocatalysts from 0.1 to 0.21V at different scan rates in 1.0 M KOH aqueous solution. (f) The corresponding fitting liner curves of the current density versus scan rate.



Fig. S20. (a, b) SEM images and (c) elemental mapping images of Pt/A-NiCo LDH catalyst after stability testing for 40 h.



Fig. S21. Atomic configurations of (a) Pt/A-NiCo LDH, (d) Ir/A-NiCo LDH and (g)
Rh/A-NiCo LDH. Adsorption configurations of M\*-H-OH on three active sites from the base plane: (b) Pt/A-NiCo LDH, (e) Ir/A-NiCo LDH and (h) Rh/A-NiCo LDH.
Adsorption configurations of M\*-H on the sites of (c) Pt/A-NiCo LDH, (f) Ir/A-NiCo LDH and (i) Rh/A-NiCo LDH.



Fig. S22. The work function of Pt/A-NiCo LDH.



Fig. S23. The work function of Ir/A-NiCo LDH.



Fig. S24. The work function of Rh/A-NiCo LDH.

**Table S1** Contents of noble metal single atoms (Pt, Ir and Rh) in the catalysts, as

 deduced from ICP-OES analysis.

Catalysts	Noble metal single atoms contents (%)
Pt/A-NiCo LDH	1.97
Ir/A-NiCo LDH	2.64
Rh/A-NiCo LDH	2.1

Catalysts	Overpotential	Tafel slop
	@ 10mA cm <sup>-2</sup>	$(mV dec^{-1})$
This work	16	38.8
Ir-NiCo LDH <sup>5</sup>	21	33.2
NiVIr LDH <sup>6</sup>	41	35.9
Rh/NiFe LDH <sup>7</sup>	58	81.3
Ni/Ni(OH) <sub>2</sub> <sup>8</sup>	77	53
Pt-NiRu OH <sup>9</sup>	38	39
Ce/CoFe LDH <sup>10</sup>	73	69
ECM@Ru <sup>11</sup>	63	47
Ru/NiV LDH <sup>12</sup>	135	111
Ni <sub>5</sub> Co <sub>3</sub> Mo-OH <sup>13</sup>	52	59
Pt/NiFe-ED <sup>14</sup>	17	45
P-Ru-CoNi-LDH <sup>15</sup>	29	41.3
NiFeRu-LDH <sup>16</sup>	29	31

Table S2. Comparison of HER activity data for LDH-based electrocatalysts.

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