Supporting Information

Atomically dispersed Rh-doped NiFe layered double hydroxides: precise location of Rh and promoting hydrazine electrooxidation properties

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Section 1. Experimental Detail

EXPERIMENTAL SECTION

Materials. Ni(NO₃)₂·6H₂O (99%), Fe(NO₃)₃·9H₂O (99%), RhCl₃·3H₂O and NaOH (>98%) were all of analytical grade and obtained from Energy Chemical and were used directly without any further purification. N₂H₄·H₂O (80%) was purchased from Beijing Chemical Reagents Company.

Synthesis of NiFe. The NiFe was synthesized using a coprecipitation method according to the reference. A 20.0 ml solution composed 0.66 mmol Ni(NO₃)₂· $6H_2O$ and 0.33 mmol Fe(NO₃)₃· $9H_2O$ was added drop by drop to a three-necked flask with 20 ml deionized water by a peristaltic pump under magnetic stirring at 80 °C. In the meantime, a solution with 0.25 M NaOH was added to the system to maintain the pH of 10. The brown precipitates were collected by centrifugation and washed with deionized water for 3 times.

Synthesis of Bulk-NiFe. A aqueous solution composed of Ni(NO₃)₂·6H₂O (0.10 mol, 29.1 g) and Fe(NO₃)₃·9H₂O (0.05 mol, 20.20 g) in 70.0 mL deionized water was added drop by drop to an aqueous solution of NaOH (0.3 mol, 12.0 g) and Na₂CO₃ (0.95 mol, 10.0 g) in 100 mL deionized water with good stirring at 30 °C. After 20 min, at the end of the addition, the flask contents were heated at 65 °C for 18 h

Synthesis of Rh/NiFe-*x* (x = 0, 0.5, 1.2, 2.7, 5.4). A 20.0 ml solution composed 0.66 mmol Ni(NO₃)₂·6H₂O, 0.33 mmol Fe(NO₃)₃·9H₂O and different amount of RhCl₃·3H₂O was added drop by drop to a three-necked flask with 20 ml deionized water

by a peristaltic pump under magnetic stirring at 80 °C . In the meantime, a solution with 0.25 M NaOH was added to the system to maintain the pH of 10. The brown precipitates were collected by centrifugation and washed with deionized water for 3 times. The x means the loading of Rh and corresponding to the RhCl₃·3H₂O amount of 0.0033 mmol, 0.0165 mmol, 0.033 mmol, 0.066 mmol, respectively.

Computational details:

The structural model of LDH used to calculate the DOS and band structure:

An ideal NiFe was built with the space group of R3-m, which contains 18 Ni atoms and 9 Fe atoms. The initial lattice parameters of 2-dimensinal layer are a = b = 3 Å. The supercell of NiFe was $3 \times 3 \times 1$ in the *a*-, *b*- and *c*- directions with lattice parameters a = b = 9 Å, c = 25.65 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. Nitrate anion not carbonate anion was chosen as equilibrium charge anion in the interlayer space to simplify the calculation. The Rh/NiFe was built by replacing a Fe atom in the first layer by Rh atoms.

The structural model of LDH used to calculate the substitution site of Rh atoms:

An ideal NiFe was built with the space group of $p\overline{3}m1$, which contains 48 Ni atoms and 24 Fe atoms. The parameters of 2-dimensinal layer are the same as above. The supercell LDH was 12 × 9 × 1 in the a-, b- and c- directions with parameters a = 36 Å, b = 18 Å, c = 8.5 Å, $\alpha = \beta = 90^{\circ}$, $\gamma = 120^{\circ}$. Then a Ni atom and a Fe atom were removed at appropriate position to form a NiFe-Matel vacancy (NiFe-Mv). Rh atom was filled in the Ni vacancy and Fe vacancy respectively to form a Rh/NiFe-Niv and Rh/NiFe-Fev.

Computational method:

The first principles density functional theory plus Hubbard U (DFT + U) calculation in this work were performed using the CASTEP module in Material Studio software package¹. The values of $U - J (U_{eff})$ were 3.80 eV for Ni²⁺, 4.30 for Fe³⁺, respectively²⁻ ⁴. The Perdew-Burke-Ernzerhof (PBE) functional in generalized gradient approximation (GGA) was used to describe the exchange and correlation⁵ and the ultrasoft pseudopotential were applied to describe the ionic cores to improve transferability and reduce the number of plane waves required in the expansion of the Kohn-Sham orbitals. The potential energy surface was searched with Broyden-letcher-Goldfarb-Shanno (BFGS) algorithm⁶. The cutoff energy was set as 381.0 eV to balance the cost and effectiveness⁷. The geometry optimization was based on the following points: (1) an energy tolerance of 5.0×10^{-5} eV/atom, (2) a maximum displacement tolerance of 5.0×10^{-3} Å, and (3) a maximum force tolerance of 0.1 eV/Å.

XANES spectra were calculated by ab initio simulations using the FDMNES package. Comparing the result calculated using finite-difference method (FDM) and multiple scattering theory (MST) with experimental data, we implemented FDM in the FDMNES code since the full potential method is more suitable to deal with distorted structures. Then a 6 Å cluster radius was calculated to save CPU resources and time. To take into account the core-hole lifetime and other multielectronic phenomena occurring in the absorption process, a convolution procedure was applied to all calculated spectra presented in this work.

Section 2. Supporting Figures and Tables



Figure S1. Schematic illustration of M^{3+} ions dispersed by M^{2+} in LDHs with the ratio of M^{2+}/M^{3+}

=2 and surface OH groups.



Figure S2. The two different models of our previous works.

By involving Ru and Pd into the LDHs using the same synthetic method, we found they have showed very different location, in which the Ru atoms are precisely located above the trivalent Fe site of the NiFe LDHs layer in the single atoms format (Chem. Sci., 2019, 10, 378-384.), while the Pd was demonstrated to be located on the layer of CoAl LDH in the form of nanoparticles (J. Energy Chem., 2020, 46, 1-7).



Figure S3. The Fourier-transform infrared (FT-IR) spectrum for NiFe, Rh/NiFe-0.5, Rh/NiFe-1.2, Rh/NiFe-2.7, Rh/NiFe-5.4.



Figure S4. The HRTEM image of Rh/NiFe-5.4 with different ranges.



Figure S5. k^3 -weight $\chi(k)$ function of EXAFS spectra (without phase correction) for Ni K-edge and Fe K-edge of NiFe, Rh K-edge of Rh/NiFe-1.2 and Rh/NiFe-5.4. To contrast the second shell of Rh, Nianalyzed and Fe.



Figure S6. a)Top view of the structures of NiFe; b)WT-EXAFS of NiFe.

Sample	Shell	Ν	R[Å]	$\sigma^2 [10^{-3} \text{\AA}^2]$	$\Delta \mathbf{E_0}$	R-factor (10 ⁻³)
Rh/NiFe-5.4	Rh-O	5.64	2.05	3.0	7.2	3.4

Table S1. Local structure parameters around Rh estimated by EXAFS analysis

N, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye-Waller factor value; E_0 , inner potential correction to account for the difference in the inner potential between the sample and the reference compound.



Total energy = -190288.60 eV

Figure S7. The calculation of substitution sites of Rh. a) The NiFe model with two types vacancies. (noted NiFe-Mv) b) The Rh/NiFe-Niv model. c) The Rh/NiFe-Fev model.



Figure S8. a) Ni K-edge XANES spectra; b) Ni K-edge EXAFS oscillation functions $k^3\chi$; c) magnitude of k^3 -weighted FT of Ni K-edge EXAFS spectra; d) Fe K-edge XANES spectra; e) Fe K-edge EXAFS oscillation functions $k^3\chi$; f) magnitude of k^3 -weighted FT of Fe K-edge EXAFS spectra.



Figure S9. Ni K-edge EXAFS fitting results for Rh/NiFe-*x* catalysts with different Rh loadings. Fitting details for Ni K-edge EXAFS spectra obtained for NiFe (a, b), Rh/NiFe-1.2 (c, d) and Rh/NiFe-5.4 (e, f).

Sample	Shell	Ν	<i>R</i> [Å]	$\sigma^{2}[10^{-3}\text{\AA}^{2}]$	ΔE_0	R-factor (10 ⁻³)	
Bulk-NiFe	Ni-O	6.00	2.05	7.1	-3.9	2 1	
	Ni-M	6.00	3.10	7.2	-0.5	5.1	
NiFe	Ni-O	5.77	2.05	7.4	-3.9	2.1	
	Ni-M	5.30	3.10	8.6	0.5		
Rh/NiFe-1.2	Ni-O	5.66	2.05	7.4	-3.9	2.6	
	Ni-M	5.10	3.10	8.5	0.1		
Rh/NiFe-5.4	Ni-O	5.54	2.05	7.4	-3.1	3.7	
	Ni-M	5.13	3.10	9.2	1.0		

Table S2. Local structure parameters around Ni estimated by EXAFS analysis

N, coordination number; *R*, distance between absorber and backscatter atoms; σ^2 , Debye-Waller factor value; E_0 , inner potential correction to account for the difference in the inner potential between the sample and the reference compound.



Figure S10. Chemical state information of Rh/NiFe-*x* a) Ni 2p XPS spectra of Rh/NiFe-*x*; b) Fe 2p XPS spectra of Rh/NiFe-*x*; c) Rh 3d XPS spectra of Rh/NiFe-*x*; d) O 1s XPS spectra of Rh/NiFe-

x.



Figure S11. The XRD and FT-IR of Bulk-NiFe.



Figure S12. The amount of gas theoretically calculated and experimentally measured versus time for hydrazine electrooxidation of Rh/NiFe-5.4



Figure **S13.** The comparison of activity with decreasing amount of Rh in NiFe LDH. The LSV curves of NiFe with different loading amount of Rh, 0.5 wt%, 1.2 wt% and 5.4 wt%, respectively.



Figure **S14.** The comparison of activity with the increase of Rh in NiFe LDH. The LSV curves of NiFe with different loading amount of Rh, 5.4 wt%, 10.5 wt% and 12.4 wt%, respectively.



Figure S15. Schematic structure model and the corresponding calculated band structure for NiFe (a, b) and Rh/NiFe (c, d). G (0, 0, 0), F (0, 1/2, 0), Q (0, 1/2, 1/2), and Z (0, 0, 1/2) are the selected reciprocal points in the first BZ.

The direct energy gap was approximately 0.623 eV for Rh/NiFe, much lower than that of NiFe (1.268 eV)



Figure S16. Total and partial electronic density of states (TDOS and PDOS) for NiFe.



Figure S17. Total and partial electronic density of states (TDOS and PDOS) for Rh/NiFe.

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