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Supplementary information

2D-structured V-doped Ni(Co,Fe) phosphides with enhanced charge transfer and reactive sites for highly efficient overall water splitting electrocatalysts

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Experimental methods

Chemicals and reagents

Ni(NO₃)₂•6H₂O (99.999%, Sigma-Aldrich), Co(NO₃)₂•6H₂O (98%, Sigma-Aldrich), Fe(NO₃)₃·9H₂O (98%, Sigma-Aldrich), VCl₃ (99%, Alfa-Aesar), N,N-dimethylformamide (DMF, 99.8%, Sigma-Aldrich), hydrochloric acid (36.5 w%, Matsunoen Chemicals) and ethanol (99.5%, Sigma-Aldrich) were used without further purification.

Synthesis of 2D structured NiCo/NiCoV LDHs

First, Ni Foam (4 × 3 cm² size, acting as a conductive electrode) was washed with HCl (used to remove the naturally occurring nickel oxide layer on the Ni foam surface), DI water, and ethanol for 10 minutes each under ultrasonication and dried immediately before the precursor solution was prepared. Then, 0.25 mmol of Ni(NO₃)₂·6H₂O, 0.05 mmol of Co(NO₃)₃·6H₂O, and 0.01 mmol of VCl₃ were dissolved in a mixed solution of 30 mL DI water and 15 mL DMF in that order. At this time, each dissolution process went through vigorous stirring for more than 20 min. Next, the precursor solution was put into a 110 mL volume of Teflon-lined stainless steel autoclave, and the prepared Ni foam was immersed in the solution. After sealing, the autoclave was heated to 120 °C and held for 14 h, and then the temperature was sequentially raised to 160 °C and maintained for 6 h. Then, the sample was cleaned with ethanol several times and dried in a 60 °C oven. NiCo LDHs were also synthesized using the same solution without adding VCl₃.

Synthesis of 2D structured NiFe/NiFeV LDHs

NiFeV LDH was also synthesized using almost the same method as NiCoV LDH. To make the precursor solution, $0.027 \text{ mmol of Ni}(NO_3)_2 \cdot 6H_2O$, $0.045 \text{ mmol of Fe}(NO_3)_3 \cdot 9H_2O$, and 0.045 mmolof VCl₃ were dissolved in the 45 mL mixed solution of DI water and DMF with the same volume ratio mentioned above. Next, the solution was put into a 110 mL volume of Teflon-lined stainless steel autoclave, and the Ni foam prepared in the same way as above was immersed in the solution. After sealing, the autoclave was heated to 120 °C and held for 15 h, and then the temperature was raised to 160 °C and maintained for 8 h. Then, the sample was cleaned with ethanol several times and dried in a 60 °C oven. NiFe LDHs were also synthesized using the same solution without adding VCl₃.

Synthesis of 2D structured NiCoP/NiCoVP/NiFeP/NiFeVP

All phosphide catalysts used in the experiment were synthesized using the same method as follows. The synthesized LDH catalyst was placed on the downstream side of a two-zone furnace, and 1 g of $NaH_2PO_2 \cdot H_2O$ was placed on the upstream side. During purging with Ar gas at a rate of 200 sccm, the P precursor and LDH were heated to 300 °C at a rate of 10 °C min⁻¹ and kept for 1 h. After cooling naturally to room temperature, the phosphide catalyst was obtained.

Electrochémical méasurements

Field emission-scanning electron microscopy (FE-SEM) (XL30S, Philips and JSM 7800F PRIME with Dual EDS) and high-resolution field emission-transmission electron microscopy (JEM-2200FS with image Cs-corrector) were used to obtain the images, and XRD (Max-2500 V, RIGAKU) was used for diffraction patterns. XPS studies were performed by LAB250 (VG scientific) with a monochromatic Al K alpha X-ray source at 15 kV.

Electrochemical measurements

All electrochemical measurements were performed in 1 M KOH (pH 14). In addition, all measured potentials were converted to reversible hydrogen electrode (RHE) values ($V_{RHE} = 0.0591 \times 14 \text{ (pH)} + 0.132 \text{ (V}_{Hg/HgO}) + V_{measured}$) without iR correction. Linear sweep voltammetry (LSV) was performed with a scan rate of 10 mV·s⁻¹ on a three-electrode system using a graphite rod as a counter electrode and a Hg/HgO electrode as a reference electrode. All LSV curves were collected after catalytic activation of 100 cyclic voltammetry (CV) cycles (-0.5 to 0 V_{RHE} for HER & 1.23 to 1.73 V_{RHE} for OER) with a scan rate of 50 mV·s⁻¹. The stability of the HER and OER catalysts was evaluated by CV and V-t tests on the same three-electrode system. CV was performed for 1000 cycles with a scan rate of 50 mV·s⁻¹.

impedance spectroscopy (EIS) was performed with an AC voltage amplitude of 5 mV within the frequency range from 0.1 Hz to 100 kHz and 0–0.3 V overpotential of HER and OER. To determine the double layer capacitance (C_{dl}), the nonfaradaic capacitive current was measured through CV in the nonfaradaic region ($0.2 \sim 0.4 V_{RHE}$ for HER and $1.13 \sim 1.23 V_{RHE}$ for OER) at scan rates of 20, 40, 60, 80, 100 and 120 mV s⁻¹. If the capacitive current ($I_{DL} = (I_{anodic} - I_{cathodic})/2$) and the scan rate (v) fit linearly, the slope is the C_{DL} of the catalyst. For the overall water splitting system, LSV and V-t tests were performed on a two-electrode system using an OER catalyst at the working electrode and a HER catalyst at the counter electrode.

Gas chromatography was carried out in specially designed flasks that were prevented from leaking gas with rubber septa. The generated gas was collected using a syringe (100 μ L, Hamilton) and injected into a gas chromatograph (HP 6890 Series, HEWLETT PACKARD) with a column (Mol Sieve 5A, SUPELCO analytical)

Turnover frequency calculations

The TOF values were calculated using the following equation:

$$TOF = \frac{J \times A \times N_A}{n \times F \times m}$$

where, *J* is the current density (iR corrected, A·cm⁻²), *A* is the surface area of the working electrode (1 cm²), N_A is the Avogadro constant (6.02 × 10²³ number of atoms per mole), *n* is the number transferred electron during HER and OER equation (2 and 4 for each), *F* is the faraday constant (96485 C·mol⁻¹), and the *m* is the number of the active sites.

To calculate *m*, we referred to the crystal structures of NiCoP and NiCoVP which were used for DFT calculation. Taking NiCoVP as an example, the maximum number of surface active sites can be calculated as following:

of surface active sites =
$$\left(\frac{17 \text{ atoms per unit cell}}{204.91 \text{ Å}^3 \text{ per unit cell}}\right)^{\frac{2}{3}} \times A_{ECSA} = 1.91 \times 10^{15} \frac{atoms}{cm^2} \times A_{ECSA}$$



204.13 Å³

 $1.94 \times 10^{15} \frac{atoms}{cm^2} \times A_{ECSA}$ For Similarly, the number of active sites of NiCoP was calculated as NiCo LDH and NiCoV LDH, we referred to the previously reported values of $8.70 \times 10^{14} \frac{atoms}{cm^2} \times A_{ECSA_{11}}$

For the NiFe based OER catalysts, both LDH and phosphide materials changed their structure to hydroxide during OER reaction, we referred to same crystral structures which were used in DFT calculation. Through calculation similar to HER catalyst, NiFe LDH and NiFeP had $7.68 \times 10^{14} \frac{atoms}{cm^2} \times A_{ECSA}$ NiFeV LDH NiFeVP calculated and was as $7.64 \times 10^{15} \frac{atoms}{cm^2} \times A_{ECSA}$

Computational measurements

All DFT calculations were carried out by the Vienna ab initio Simulation Package (VASP)^{1,2}. The projector augmented wave (PAW) formula with spin polarization^{3,4}. During the structure optimization, the convergence criterion of total energy was set to 2×10^{-4} eV, and the atoms were relaxed until the force acting on each atom was less than 0.03 eV/Å. Plane-wave cutoff energy of 400 eV was used in all geometry optimization calculations. Brillouin-zone sampling was sampled with $3 \times 3 \times 5$ and $6 \times 6 \times 4$ gamma points for bulk NiCo(V)P and NiFe(V)(OH)₂ optimization, respectively. The bottom two layers of four layers were fixed in the slab model, and each slab model was separated from its neighbors by a sufficiently thick vacuum layer (~10 Å). The Gibbs free energies of the alkaline HER were calculated by correcting the DFT energy with zero-point energy and entropy via

$$\Delta G = \Delta E + \Delta Z P E - T \Delta S$$

where *E* is the DFT total energy, *ZPE* is the zero zero-point energy, *T* is the environmental temperature (298.15 K), and *S* is the entropy. For zero-point energy correction and entropy calculations, the vibrational frequencies were calculated by employing density functional perturbation theory. The PDOS for each element (Ni, Fe, O) was calculated and applied to equation (1) to obtain the *d*-band center (Ni, Fe) and the *p*-band center (O):



where ε is the band center, E is the energy, E_f is the Fermi level energy, and ρ is the DOS.



NiCo LDHNiCoV LDHNiCoVPFig. S1 High magnification SEM image and thickness of NiCo LDH, NiCoV LDH and NiCoVP



Fig. S2 XPS spectra of V 2p for NiCoV LDH



Fig. S3 EDX spectrum of NiCoVP measured by SEM



Fig. S4 (a) LSV curves for various Co:V ratios for NiCoVP HER catalysts and (b) CV curves during alkaine HER activation cycles.



Fig. S5 XPS spectra of Ni 2p (a, b) and P 2p (c, d) in NiCoVP before and after HER process in 1M KOH



Fig. S6 The atomic structures and their structural stability of (a) NiCoP and (b) NiCoVP with various doping position of Co and V atoms.



Fig. S7 High magnification SEM image and thickness of NiFe LDH, NiFeV LDH and NiFeVP



Fig. S8 XPS spectra of V 2p for NiFeV LDH



Fig. S9 EDX spectrum of NiFeVP measured by SEM



Fig. S10 Reverse-scan linear sweep voltammetry curves for NiFe LDH, NiFeV LDH, NiFeP, and NiFeVP at 1M KOH



Fig. S11 LSV curves for various Fe:V ratios for NiFeVP OER catalysts (a) above 1:1, (b) below 1:1 and (c) CV curves during alkaine OER activation cycles.



Fig. S12 XPS spectra of Ni 2p (a, b) and P 2p (c, d) in NiFeVP before and after OER process in 1M KOH.



Fig. S13 The atomic structures and their structural stability of (a) NiFeP and (b) NiFeVP with various doping position of Fe and V atoms.



Fig. S14 SEM images of (a) NiCoVP and (b) NiFeVP after the overall water splitting stability test for 56 h.

Table S1. Inductively coupled plasma optical emission spectrometer (ICP-OES) results for NiCoV

LDH and NiCoVP

| Samples | Co (mg) | V (mg) | Atomic ratio (Co:V) | | |
|-----------|---------|--------|------------------------|--|--|
| NiCoV LDH | 0.048 | 0.01 | 4.15:1 | | |
| NiCoVP | 0.049 | 0.009 | 4.71:1 | | |

Table S2. BET surface area of NiCo-based HER catalysts

| Catalysts | BET surface area(m ² /g) |
|-----------|-------------------------------------|
| Ni foam | 0.7058 |
| NiCo LDH | 14.4121 |
| NiCoV LDH | 13.7154 |
| NiCoP | 14.9177 |
| NiCoVP | 18.8216 |

Table S3. Turnover frequency (TOF) for NiCo-based HER catalysts at 100 mV overpotential.

| Catalysts | TOF(s ⁻¹) at η=100mV |
|-----------|----------------------------------|
| NiCo LDH | 0.25 |
| NiCoV LDH | 0.417 |
| NiCoP | 0.33 |
| NiCoVP | 0.421 |

Table S4. ICP-OES results for NiFeV LDH and NiFeVP

| Samples | Fe (mg) | V (mg) | Atomic ratio (Fe:V) | |
|-----------|---------|--------|------------------------|--|
| NiFeV LDH | 0.078 | 0.078 | 0.91:1 | |
| NiFeVP | 0.079 | 0.077 | 0.94:1 | |

Table S5. BET surface area of NiFe-based OER catalysts

| Catalysts | BET surface area(m ² /g) |
|-----------|-------------------------------------|
| NiFe LDH | 10.742 |
| NiFeV LDH | 8.437 |
| NiFeP | 11.489 |
| NiFeVP | 10.248 |
| 111 0 1 | 10.240 |

Table S6. Turnover frequency (TOF) for NiFe-based OER catalysts at 300 mV overpotential.

| Catalysts | TOF(s ⁻¹) at η=300mV |
|-----------|----------------------------------|
| NiFe LDH | 0.14 |
| NiFeV LDH | 0.437 |
| NiFeP | 0.20 |
| NiFeVP | 0.45 |

| Catalysts (HER/OER) | Substrate | η (HER) (10 mA·cm ⁻²) | η (OER) (10 mA·cm ⁻²) | OWS voltage (10 mA·cm ⁻²) | Stability | Reference |
|--|------------------|--------------------------------------|---------------------------------------|--|-----------|-----------|
| NiCoVP/NiFeVP | Ni Foam | 42 mV | 234 mV | 1.50 V | 56 h | This work |
| Ni ₃ N-VN/Ni ₃ P-VP | Ni Foam | 64 mV | 306 mV (50 mA·cm ⁻²) | 1.51 V | 100 h | 5 |
| N-NiFeVP Bifuntional | Ni Foam | 79 mV | 229 mV | 1.52 V | 100 h | 6 |
| MoP-Ni ₂ P Bifunctional | Ni Foam | 75 mV | 309 mV (20 mA·cm ⁻²) | 1.55 V | 24 h | 7 |
| O-V-Ni ₂ P Bifunctional | Glassy Carbon | 108 mV | 257 mV | 1.56 V | 20 h | 8 |
| Ni ₂ P-Fe ₂ P Bifunctional | Ni Foam | 128 mV | 218 mV | 1.561 V | 48 h | 9 |
| NiFeP@NC-Ni ₂ P Bifunctional | Glassy Carbon | 257 mV | 223 mV (20 mA·cm ⁻²) | 1.57 V | 24 h | 10 |
| Ti ₃ C ₂ @mNiCoP Bifunctional | Carbon Cloath | 127 mV | 237 mV | 1.57 V | 12 h | 11 |
| NiFeSP Bifunctional | Ni Foam | 94 mV | 290 mV (50 mA · cm ⁻²) | 1.58 V | 20 h | 12 |
| NiCoP Bifunctional | Ni Foam | 107 mV | 270 mV | 1.62 V | 20 h | 13 |
| Ni-P Bifunctional | Ni Foam | 121 mV | 232 mV | 1.65 V | 100 h | 14 |

Table S7. Electrocatalytic water splitting activity comparison with other transition metal phosphides reported.

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