Supplementary Information

Effective electronic tuning of Pt single atoms via heterogeneous atomic coordination of (Co,Ni)(OH)₂ for efficient hydrogen evolution

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¹ These authors contributed equally to this work.
Experimental methods

Materials preparation

The (Co,Ni)(OH)$_2$/C catalyst was prepared via a precipitation method. Firstly, the same amount of NiCl$_2$·6H$_2$O and CoCl$_2$·6H$_2$O precursors was mixed into 82.5 mL of deionized water (N$_2$-saturated) and stirred for 0.5 h at room temperature. Then, 12.5 mL ethanol was added to form a uniform coordination compound. After 10 min, Carbon (0.3 g) was added to the solution. The solution was kept N$_2$-saturated by continuing bubbled N$_2$. The as-prepared N$_2$-saturated NaOH (99.99%) solution was injected into the mixed solution quickly to deposit (Co,Ni)(OH)$_2$ on carbon. After vigorous stirring for 10 h, the (Co,Ni)(OH)$_2$/C catalyst was obtained. After being washed with the deionized water several times, the (Co,Ni)(OH)$_2$/C was loaded on carbon paper. After carbon paper was dried naturally, it was immersed in 1 mmol·L$^{-1}$ H$_2$PtCl$_6$ solution, and the series of the Pt/(Co,Ni)(OH)$_2$/C catalysts were synthesized by an electrodeposition strategy. The electrodeposition experiments were conducted with the standard three-electrode system using CHI 760e Instrument. Carbon paper (1 × 1 cm$^2$) covered catalysts (3 mg, ethanol: water = 9:1, ultrasound for 30 min, dropped with 40 uL 0.25 wt% Nafion solution) were used as the working electrode, and 1 mmol·L$^{-1}$ H$_2$PtCl$_6$ solution as the electrolyte for the Pt deposition. The saturated calomel electrode (SCE) with a salt bridge was used as the reference electrode, a graphite rod was applied as the counter electrode. The constant potentials of the electrodeposition process were -0.8 V (vs. SCE) for 10, 20, and 30 s, respectively. The Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C, and Pt$_1$/C were prepared by controlling the same electrodeposition time of 20 s. The carbon paper electrodeposited with Pt was washed with ultrapure water several times. After drying at room temperature, it was employed for the electrochemical measurements directly.

Characterizations

Inductively coupled plasma optical emission spectrometry (ICP-OES) was performed on an Agilent 730 to accurately measure the practical content of the metals (e.g., Pt, Co, Ni) in the samples. Aberration-corrected high-resolution transmission electron microscopy (Titan G2 60-300) was applied to reveal the morphology and nanostructure of different catalysts at 300 kV acceleration voltage. The Titan G2 60-300 was also applied to acquire the images of AC-STEM-EDS chemical elemental mapping of C, O, Ni, Co, and Pt with an acceleration voltage of 300 kV. The phase composition and structure of the catalysts were
acquired through XRD measurements (Rigaku Ultima IV X-ray diffractometer) with Cu $K_a$ as an X-ray source ($\lambda$=0.15406 nm). The surface element's valence state of the catalysts was analyzed via X-ray photoelectron spectroscopy spectrum on a PHI Quantum 200 to obtain the metal composition and atomic valence states of the surface. In the measurements, Al $K_a$ ($h\nu$=1486.6 eV) was adopted as the target source to correct the binding energy of the catalysts, with the binding energy of C 1s (284.6eV) as the internal standard.

**Operando Raman spectra**

The Operando Raman measurements were carried out employing a Horiba HR-800 Raman microspectrometer. The 1 × 1 cm$^2$ carbon paper-covered catalysts were adopted as the working electrode, a Hg/HgO was employed as reference electrodes and the counter electrodes were a graphite rod. A two-compartment electrochemical cell equipped with a proton exchange membrane (Nafion 117, Sigma-Aldrich) was used in a 1.0 M KOH solution. Combining with a CHI 650 electrochemical workstation, Operando Raman spectra at OCP and different applied potential (vs. Hg/HgO) for Pt$_1$/(Co,Ni)(OH)$_2$/C and Pt$_1$/C were recorded with a typical electrochemical Raman spectroscopy setup in 1.0 M KOH.

**Electrochemical measurements**

All electrochemical measurements were carried out by electrochemical workstation CHI 760E using a three-electrode system with a carbon rod as the counter electrode, a saturated calomel electrode as a reference electrode, and carbon paper uniformly covered with an as-prepared catalyst as the working electrode. The air-blowing of N$_2$ to 1.0 M KOH (99.99%) electrolyte was performed for more than 20 mins to remove the oxygen in the 1.0 M KOH electrolyte preceding the electrochemical measurements. For the evaluation of double-layer capacitance ($C_{dl}$) towards different materials, the cyclic voltammetry (CV) was estimated at the potential range of 0.2 to 0.4 V (vs. RHE) at different scan rates from 20 to 100 mV·s$^{-1}$. Besides, linear sweep voltammetry (LSV) curves were recorded with the potential from -0.6 to 0 V (vs. RHE) by a sweep rate of 5 mV·s$^{-1}$. After the open-circuit voltage was determined, electrochemical impedance spectroscopy (EIS) was performed with a potential amplitude from 100 to 1.0 kHz to obtain the Nyquist plots. Moreover, two typical methods were both carried out to appraise the stability of the catalysts. One was the continuous cyclic voltammetry, which was performed for 20000 cycles at the sweep rate of 50 mV·s$^{-1}$ and the other was the chronoamperometry at 100 mA·cm$^{-2}$ for 24 h.
Computational method

All the density functional theory (DFT) calculations were performed via the Vienna Ab initio Simulation Package (VASP),\textsuperscript{1-3} and the projector-augmented plane wave (PAW) pseudopotentials were used for the elements involved.\textsuperscript{4} The generalized gradient approximation (GGA) of Perdew, Burke, and Ernzerhof (PBE) was used to treat the exchange-correlation of electrons.\textsuperscript{5} The models of (Co,Ni)(OH)\textsubscript{2}, (Co,Ni)(OH)\textsubscript{2} adsorbed with Pt single atom (Pt\textsubscript{1}/(Co,Ni)(OH)\textsubscript{2}) and Pt(111) slabs calculated in this study are shown in Fig.S17-19. The models for Pt\textsubscript{1}/Co(OH)\textsubscript{2} and Pt\textsubscript{1}/Ni(OH)\textsubscript{2} are the same as the Pt\textsubscript{1}/(Co,Ni)(OH)\textsubscript{2} except for the elements in the hydroxides. The (001) facet is selected for all hydroxides in this study since they are layered structures along the (001) direction. A vacuum region larger than 15 Å was added along the direction normal to the slab plane to avoid the interaction between periodic supercells. The electron wave function was expanded in plane waves and a cutoff energy of 500 eV was selected. The Monkhorst-Pack meshes of (3×3×1) were adopted for the Brillouin zone (BZ) of the slabs.\textsuperscript{6} The convergence in the energy and force were set to 10\textsuperscript{-4} eV and 0.01 eV/Å, respectively.

In this study, the hydrogen binding energy in Fig. 3i was calculated as:

\[
\Delta E_{H} = E(*H) - E(H^+ + e^-) - E(*)
\]  

(1)

where \(E(*H), E(H^+ + e^-)\) and \(E(*)\) were the total energy directly obtained by DFT calculations. \(E(H^+ + e^-) = 1/2E(H_2)\) at 0 V vs. reversible hydrogen electrode (RHE) according to the computational hydrogen electrode (CHE) model which was proposed by Nørskov \textit{et al.}\textsuperscript{7,8}

The free energies of \(H_2O(l)\) and \(H_2(g)\) were used as references for the calculation of the free energies of reaction intermediates. The adsorption energy for the reaction intermediate is calculated as follows:\textsuperscript{9}

\[
\Delta G = \Delta E_{Total} + \Delta E_{ZEP} - T\Delta S + \Delta G_s
\]  

(2)

where \(\Delta E_{Total}\) is the calculated adsorption total energy by DFT, \(\Delta E_{ZEP}\) is zero-point energy, \(\Delta S\) is entropy, and \(\Delta G_s\) is solvation energy.\textsuperscript{10-13}

Calculation of the surface density of single atoms and TOF of the catalysts
We calculated the surface density of single atoms (0.58 Pt atoms nm\(^{-2}\)) based on Pt loading measured by ICP-OES and the specific surface area of the catalyst. This method of estimating the density of single atoms has also been adopted by some recent publications: (Adv. Funct. Mater., 2021, 31, 2104343; ACS Catal., 2019, 9, 3978-3990; Nat. Commun., 2019, 10, 234). The calculation process is given as follows:

Step 1. Calculation of the amount of Pt material on the electrode surface = \((3 \times 10^{-3} \text{g} \times 1.41 \text{wt\%})/(195.05 \text{g/mol}) = 1.8057 \times 10^{-7} \text{mol}\)

\((3 \times 10^{-3} \text{g} = \text{sample weight}, \text{Pt loading} = 1.41 \text{wt\%, molar mass of Pt} = 195.05 \text{g/mol})\)

Step 2. Calculation of the specific surface area of Pt\(_1\) (electrochemical active area) in Pt\(_1\)/(Co,Ni)(OH)\(_2\)/C = \((178.9 - 89.8)/0.04 = 2227.5 \text{ cm}^2 = 2.2275 \times 10^{17} \text{ nm}^2\),

\((178.9 \text{ mF cm}^{-2} \text{ and } 89.8 \text{ mF cm}^{-2}\text{are the } C_{dl\_Pt}(\text{Co,Ni})(OH)\(_2\)/C \text{ and } (\text{Co,Ni})(OH)\(_2\)/C, \text{respectively; the difference of } [C_{dl\_Pt}/(\text{Co,Ni})(OH)\(_2\)/C - C_{dl\_}(\text{Co,Ni})(OH)\(_2\)/C ] \text{represents the contribution of Pt}_1 \text{to ECSA, the Cs of carbon-based materials} = 0.04 \text{ mF cm}^{-2}\))

Step 3. Calculation of the surface (area) density of the single atoms = \(1.8057 \times 10^{-7} \text{ mol} \times 6.02 \times 10^{23}/(2.2275 \times 10^{17} \text{ nm}^2) = 0.58 \text{ Pt atoms nm}^{-2} = 5.8 \times 10^{13} \text{ Pt atoms cm}^{-2}\)

\((1.8057 \times 10^{-7} \text{ mol refers to the amount of Pt material on the electrode surface, } 6.02 \times 10^{23} \text{ was Avogadro constant (the number of Pt atoms in 1 mol Pt), } 2.2275 \times 10^{17} \text{ nm}^2 \text{represents the specific surface area of Pt}_1\))

The calculation method of turnover frequency (TOF, s\(^{-1}\)) of single-atom catalysts for the HER:
The turnover frequency (TOF, s\(^{-1}\)) of the catalysts for the HER, defined as the hydrogen evolution reaction (HER) rate per active site and per time, was derived from the following equation (1).\(^{14-16}\)

\[
\text{TOF (s}^{-1}\text{)} = \left\{ \frac{\text{number of total hydrogen / cm}^2 \text{ of geometric area}}{\text{number of total active actives of / cm}^2 \text{ geometric area}} \right\}
\]

Here, the current density (j) was derived from the current generated during the HER. The total number of hydrogens turn overs were calculated from the current density according to the following equation (2), and the TOF (s\(^{-1}\)) was obtained by equation (3).
\[
\text{No. } H_2 = \frac{|j| \ mA}{cm^2} \left( \frac{1 \ C \ cm^{-1}}{1000 \ mA} \right) \left( \frac{1 \ mol \ e^-}{96485.3 \ C} \right) \left( \frac{1 \ mol \ H_2}{2 \ mol \ e^-} \right) \left( \frac{6.022 \times 10^{23} \ H_2 \ molecules}{1 \ mol} \right)
\]

\[
= |j| \times 3.12068 \times 10^{15} \left( \frac{H_2/s}{cm^2 \ per \ cm^2} \right) \frac{mA}{cm^2}
\]

(2)

\[
\text{TOF } (s^{-1}) = (|j| \times 3.12068 \times 10^{15} \left( \frac{H_2/s}{cm^2 \ per \ cm^2} \right) \frac{mA}{cm^2}) / N_{active}
\]

(3)

For the single-atom catalyst model, the total number of Pt single-atoms on the electrode surface was obtained by the estimated ICP-OES analysis. Every two Pt single atoms worked as an HER active site in DFT calculation. Thus, the total number of active actives geometric area (cm\(^{-2}\)) \(N_{active}\) was derived from the following equation (4).

\[
N_{active} = \frac{1}{2} \times \left\{ NA \times \left( \frac{m \times S \times \text{wt\%}}{M} \right) \right\}
\]

(4)

Here, the \(NA\) was Avogadro constant (the number of Pt atoms in 1 mol Pt, \(6.022 \times 10^{23}\)), \(m\) is the loading of the catalyst on the electrode (3\(*10^{-3}\) g cm\(^{-2}\) in our case), \(S\) is the geometric surface area of the working electrode (1 cm\(^2\) in this work), The \(\text{wt\%}\) of Pt was estimated by ICP-OES analysis, \(M\) is the molar mass of Pt = 195.05 g/mol
Table S1 Metal contents and atomic ratios in different catalysts measured by ICP-OES.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Metal loading (wt%)</th>
<th>Atomic ratios</th>
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<tr>
<td></td>
<td></td>
<td>Pt%</td>
<td>Co%</td>
</tr>
<tr>
<td>1</td>
<td>Pt/(Co,Ni)(OH)₂/C-10 s</td>
<td>0.81</td>
<td>6.28</td>
</tr>
<tr>
<td>2</td>
<td>Pt₁/(Co,Ni)(OH)₂/C-20 s</td>
<td>1.41</td>
<td>6.26</td>
</tr>
<tr>
<td>3</td>
<td>Pt/(Co,Ni)(OH)₂/C-30 s</td>
<td>3.67</td>
<td>6.25</td>
</tr>
<tr>
<td>4</td>
<td>Pt₁/Co(OH)₂/C</td>
<td>1.63</td>
<td>12.32</td>
</tr>
<tr>
<td>5</td>
<td>Pt₁/Ni(OH)₂/C</td>
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</tr>
<tr>
<td>6</td>
<td>Pt₁/C</td>
<td>1.85</td>
<td>-</td>
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</tbody>
</table>
Fig. S1 The spacing of 0.23 nm matches well with the spacing between neighboring (101) planes of (101) for (Co,Ni)(OH)$_2$. 
Fig. S2 (a) SAED patterns showing diffraction spots from (101) and (111) lattice planes of hydroxide. (b) SAED patterns
for amorphous carbon support.
Fig. S3 FT-IR spectrum of Pt₁/(Co,Ni)(OH)₂/C sample. To further confirm the presence of the hydroxide phase of Pt₁/(Co,Ni)(OH)₂/C sample, the FT-IR analysis was conducted. According to the FT-IR results and the references, the infrared spectra were accurately attributed and the existence of hydroxides was confirmed. (*Int. J. Hydrogen Energy, 2021, 46, 22789-22798. Nanoscale, 2019, 11, 12655-12671. Electrochim. Acta* 2021, 368, 137633. *Chem. Eng. J.* 2020, 390, 124525.)
Fig. S4 The HER polarization curves: (a) 0.82wt% Pt/(Co,Ni)(OH)$_2$/C, Pt$_1$/((Co,Ni)(OH)$_2$/C, 3.67wt% Pt/(Co,Ni)(OH)$_2$/C, and (Co,Ni)(OH)$_2$/C; (b) Pt$_1$/((Co,Ni)(OH)$_2$/C, Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C, Pt$_1$/C, and commercial 20 wt% Pt/C, with $iR$ compensation (98 %) in an N$_2$-saturated 1.0 M KOH solution at a current density of 10 mA cm$^{-2}$, the scan rate of 5 mV s$^{-1}$; (c) Tafel plots of Pt$_1$/((Co,Ni)(OH)$_2$/C, Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C; (d) Comparison of the overpotentials of the as-prepared catalysts, along with those of the commercial 20 wt% Pt/C, at 10 and 100 mA·cm$^{-2}$, respectively.
Fig. S5 HER polarization curves at a high current density range to 400 mA cm$^{-2}$: (a) as-synthesised catalysts of different Pt loading; and (b) Pt$_{1}$/catalysts on different types of support. The stability of the Pt$_{1}/$(Co,Ni)(OH)$_2$/C is clearly shown.
**Fig. S6** The HER mass activity (normalized by the loading of Pt) towards the as-obtained catalysts and commercial 20 wt% Pt/C with 98% $iR$ compensation at -0.09 V.
**Fig. S7** Nyquist plots of as-obtained Pt Single atom catalysts and (Co,Ni)(OH)$_2$/C substrate in 1.0 M KOH solution.
Fig. S8 (a) Nyquist plots; (b) Tafel plots; Linear fitting of the capacitive current versus the CV scanning rate: (c) 0.82 wt% Pt/(Co,Ni)(OH)$_2$/C, Pt$_1$/(Co,Ni)(OH)$_2$/C, and 3.67 wt% Pt/(Co,Ni)(OH)$_2$/C, and (d) Pt$_1$/(Co,Ni)(OH)$_2$/C, Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C, and (Co,Ni)(OH)$_2$/C.

Pt/(Co,Ni)(OH)$_2$/C, Pt$_1$/(Co,Ni)(OH)$_2$/C, and 3.67 wt% Pt/(Co,Ni)(OH)$_2$/C, and (d) Pt$_1$/(Co,Ni)(OH)$_2$/C, Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C, and (Co,Ni)(OH)$_2$/C.
Fig. S9 CV curves of (a) 0.82 wt% Pt/(Co,Ni)(OH)$_2$/C, (b) Pt$_x$/((Co,Ni)(OH)$_2$/C, (c) 3.67 wt% Pt/(Co,Ni)(OH)$_2$/C, (d) Pt$_x$/Co(OH)$_2$/C, (e) Pt$_x$/Ni(OH)$_2$/C, and (f) (Co,Ni)(OH)$_2$/C in the region of 0.2 to 0.4 V (the Non-Faraday interval) with scanning rates from 20 to 100 mV·s$^{-1}$, used to calculate the ESCA.
Fig. S10 The ECSA normalization for all the as-prepared catalysts.
Fig. S11 (a) TOFs of the Pt$_1$/Co,Ni(OH)$_2$/C, Pt$_1$/Co(OH)$_2$/C, Pt$_1$/Ni(OH)$_2$/C, and Pt$_1$/C samples at an overpotential of 0 to 0.15 V. (b) Comparison of TOFs at an overpotential of 0.1 V.

15.4 times
Fig. S12 (a-e) The Tafel plots of the samples. (f) Volcano plot of hydrogen adsorption free energy (ΔGH*) of different metal catalysts in HER.
Fig. S13 Comparison of water dissociation energy of different reported catalysts including the Co(OH)$_2$ (0.02 eV)$^{[17]}$, Pt$_1$-C$_2$ (0.06 eV)$^{[19]}$, Ru-doped SrTiO$_3$ (0.17 eV)$^{[19]}$, Co$_3$S$_4$ PNS$_{vac}$ (0.27 eV)$^{[20]}$, O$_x$Cu-CoPO nanowire (0.34 eV)$^{[21]}$, RhO$_2$ (0.35 eV)$^{[22]}$, α-MoC$_{1-x}$ (0.51 eV)$^{[23]}$, Ru-N$_4$ (0.550 eV)$^{[24]}$, Mo exposed NiMoP (0.56 eV)$^{[25]}$, pyridinic-N-MoP (0.58 eV)$^{[26]}$, NiO/Pt (0.58 eV)$^{[27]}$, Cr-Co$_4$N (0.58.eV)$^{[28]}$, Mn-hcp Ni (0.61 eV)$^{[29]}$, MoS$_2$/LDH (0.64 eV)$^{[30]}$, 1T-MoS$_2$/SWNT (0.79 eV)$^{[31]}$, CoNiS$_2$ (0.80 eV)$^{[32]}$, GN$_2$@RuMo (1.2 eV)$^{[33]}$, MoS$_2$/Ni(OH)$_2$ (1.83 eV)$^{[34]}$, and Ni$_3$N (2.33 eV)$^{[35]}$. 
Fig. S14 CV curves of (a) the initial Pt₁/C, (b) Pt₁/C after CP for 24 h, and (c) Pt₁/C after 20000 cycles in the region of 0.2 to 0.4 V with scan rates from 20 to 100 mV s⁻¹.
Fig. S15 CV curves of (a) the initial Pt_{20}/(Co,Ni)(OH)$_2$/C, (b) Pt$_{20}/$(Co,Ni)(OH)$_2$/C after CP for 24 h, (c) Pt$_{20}/$(Co,Ni)(OH)$_2$/C after 20000 cycles in the region of 0.2 to 0.4 V with scan rates from 20 to 100 mV s$^{-1}$. 
Fig. S16 Comparison of the effect of scanning rate at 50 and 200 mV s$^{-1}$ on the HER performance of Pt$_1$/(Co,Ni)(OH)$_2$/C; and Pt/C at 50 mV s$^{-1}$ for 5000 cycles.
Table S2 Comparison of the HER activities between Pt₁/(Co,Ni)(OH)₂/C and other reported Pt single atomic electrocatalysts.

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Electrolyte</th>
<th>PtSA loading (wt%)</th>
<th>η₁₀ (mV)</th>
<th>Tafel slope (mV dec⁻¹)</th>
<th>References</th>
</tr>
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<tbody>
<tr>
<td>Pt₁/(Co,Ni)(OH)₂/C</td>
<td>1.0 M KOH</td>
<td>1.41</td>
<td>24</td>
<td>28.7</td>
<td>This work</td>
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<tr>
<td>Pt-SA/MoSe₂</td>
<td>1.0 M KOH</td>
<td>4.70</td>
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<td>34</td>
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<tr>
<td>Pt-SA/MoS₂</td>
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<td>5.10</td>
<td>65</td>
<td>50</td>
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<tr>
<td>Pt-SA-Mn₃O₄</td>
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<td>2.00</td>
<td>24</td>
<td>54</td>
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<tr>
<td>Pt-SA-Co(OH)₂@Ag NWs</td>
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<td>2.8</td>
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<td>Pt₁/N-C</td>
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<td>2.50</td>
<td>46</td>
<td>36.8</td>
<td>Nat. Commun. 2020, 11, 1029</td>
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<td>Pt-SA-NiO/Ni</td>
<td>1.0 M KOH</td>
<td>1.14</td>
<td>26</td>
<td>27</td>
<td>Nat. Commun. 2021, 12, 3783</td>
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<tr>
<td>Pt-SA/S-C</td>
<td>0.5 M H₂SO₄</td>
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<td>Pt-SA-Co(OH)₂</td>
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<td>Pt-SA/TiO₂</td>
<td>1.0 M KOH</td>
<td>1.10</td>
<td>-</td>
<td>410</td>
<td>Chem. Eng. J. 2022, 427, 131309</td>
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<td>Mo₂TiC₂Te-PtSA</td>
<td>0.5 M H₂SO₄</td>
<td>1.20</td>
<td>30</td>
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<td>Nat. Catal. 2018, 1, 985</td>
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### Table S3 Comparison of the HER activities between Pt/(Co,Ni)(OH)$_2$/C and other reported advanced electrocatalysts.

<table>
<thead>
<tr>
<th>Electrocatalysts</th>
<th>Electrolyte</th>
<th>$\eta_{10}$ (mV)</th>
<th>$\eta_{50}$ (mV)</th>
<th>Tafel slope (mV dec$^{-1}$)</th>
<th>References</th>
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<tr>
<td>Pt/(Co,Ni)(OH)$_2$/C</td>
<td>1.0 M KOH</td>
<td>24</td>
<td>65</td>
<td>28.7</td>
<td>This work</td>
</tr>
<tr>
<td>Pt/MgO</td>
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<td>39</td>
<td>-</td>
<td>39</td>
<td>Nat. Commun. 2022, 13, 2024</td>
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<td>IrCo@N-C</td>
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<td>45</td>
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<td>80</td>
<td>Adv. Mater. 2018, 30, 1705324</td>
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<td>Pt/TiB$_2$O$_x$</td>
<td>1.0 M KOH</td>
<td>~200</td>
<td>-</td>
<td>135</td>
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<td>RuCo@N-C</td>
<td>1.0 M KOH</td>
<td>28</td>
<td>-</td>
<td>31</td>
<td>Nat. Commun. 2017, 8, 14969</td>
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<tr>
<td>Sr$_2$RuO$_4$</td>
<td>1.0 M KOH</td>
<td>61</td>
<td>-</td>
<td>51</td>
<td>Nat. Commun. 2019, 10, 149</td>
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<td>er-WS$_2$-Pt</td>
<td>1.0 M KOH</td>
<td>~48</td>
<td>-</td>
<td>65</td>
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<td>Ru@CN-0.16</td>
<td>1.0 M KOH</td>
<td>284</td>
<td>-</td>
<td>27.8</td>
<td>Energy Environ. Sci. 2018, 11, 800</td>
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<td>Pt@PCM</td>
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<td>Sci. Adv. 2018, 4, eaao6657</td>
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<td>Nano Energy 2020, 72, 104669</td>
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<td>Ru/Ni(OH)$_2$/NF</td>
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<td>J. Mater. Chem. A 2019, 7, 11062-11068</td>
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<td>101</td>
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<td>Chem. Commun. 2018, 54, 6400-6403</td>
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<td>Adv. Mater. 2018, 30, 1706279</td>
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<td>Angew. Chem. Int. Ed. 2017, 56, 11559-11564</td>
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<td>ACS Catal. 2017, 7, 7131-7135</td>
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<td>Adv. Mater. 2020, 32, 1906972</td>
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Fig. S17 Atomic structures of intermediates: (a) *H₂O, (b) *OH + *H, and (c) *H, adsorbed on (Ni,Co)(OH)₂. The red, green, blue, grey, yellow, and white balls are for O, Co, Ni, Pt, and H atoms, respectively.
Fig. S18 Atomic structures of intermediates: (a) $^*\text{H}_2\text{O}$, (b) $^*\text{OH} + ^*\text{H}$, and (c) $^*\text{H}$, adsorbed on Pt$_1$/Ni$_{0.5}$Co$_{0.5}$(OH)$_2$. The red, green, blue, grey, yellow, and white balls are for O, Co, Ni, Pt, and H atoms, respectively.
Fig. S19 Atomic structures of intermediates: (a) $^{*}\text{H}_2\text{O}$, (b) $^{*}\text{OH} + ^{*}\text{H}$ and (c) $^{*}\text{H}$, on commercial Pt(111). The yellow and white balls are for Pt, and H atoms, respectively.
**Fig. S20** Charge density difference for the adsorption of one H on Pt(111). Electrons accumulate between Pt and H and deplete on these two atoms which indicate that there is a covalent bond between them. The yellow and white balls are for Pt, and H atoms, respectively. The charge depletion and accumulation were depicted by blue and yellow isosurfaces, respectively.
Fig. S21 Charge density difference for the adsorption of one H on Pt/(Ni,Co)(OH)$_2$. Electrons accumulate (yellow) between Pt and H and deplete (blue) on the other two metallic atoms, indicating a covalent bond between them. The charge depletion and accumulation were depicted by blue and yellow isosurfaces, respectively.
**Fig. S22** Density of states for $3d$ states of Pt atoms in (a) Pt(111), (b) Pt$_1$/Ni(OH)$_2$, (c) Pt$_1$/Co(OH)$_2$ and (d) Pt$_1$/Co,Ni(OH)$_2$.

The energy levels of the $d$-band center of each Pt atom are highlighted by a red line.
References


