

Supporting Information

Superlattice ordering Pt₂CoNi intermetallic nanocatalysts with surface microstrain for efficient hydrogen electrocatalysis

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Experiment section

Materials characterization.

Energy-dispersive spectroscopy (EDS) line scanning profiles and elemental maps were recorded by JEOL JEM-F200. The aberration-corrected high angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images were collected by JEOL JEM-ARM200F. X-ray diffraction (XRD) patterns were performed using Rigaku SmartLab 9kW with Cu K α radiation ($\lambda=0.15406$ nm). Inductively coupled plasma-optical emission spectrometry (ICP-MS) was conducted using a Aglient 5110.

Electrochemical measurements.

All of the electrochemical measurements were performed on a Corrtest electrochemical workstation (CS310X) with Pt foil as a counter electrode, Hg/Hg₂SO₄ (saturated K₂SO₄) as a reference electrode. As shown in Fig. S14, the Hg/Hg₂SO₄ reference electrode was calibrated with respect to the reversible hydrogen electrode (RHE). The calibration was performed in an H₂-saturated 0.5 M H₂SO₄ solution or 0.1 M HClO₄ with Pt foil electrodes as the working and counter electrodes and

Hg/Hg₂SO₄ as the reference electrode. The average of the two potentials at which the current crossed zero was taken to be the thermodynamic potential for the hydrogen electrode reactions. Therefore, in 0.5 M H₂SO₄, E(RHE) = E(Hg/Hg₂SO₄) + 0.700 V. In 0.1 M HClO₄, E(RHE) = E(Hg/Hg₂SO₄) + 0.722 V. The catalyst ink was prepared by sonicating the mixture consisting of 1 mg catalyst, 8 μ L Nafion (5 wt%) in 192 μ L ethanol.

Electrochemical measurements of HER. The ink was drop-coated on the carbon paper with Pt loading of 0.1 mg/cm² and dried naturally. The activation was performed by a cyclic voltammetry at a scan rate of 100 mV/s for 10 cycles. Linear sweep voltammetry was then conducted in 0.5 M H₂SO₄ by sweeping the potential from 0.1 V to -1.2 V at 5 mV/s. 80% iR-correction were performed on all catalysts. Tafel slope was calculated with according to the polarization profiles. The electrochemical impedance spectrum was recorded at a constant potential with a signal amplitude of 10 mV over a frequency range from 0.1 Hz to 100 kHz. The electrochemical active surface area (ECSA) was determined through a CO stripping test. CO stripping test involved bubbling CO into 0.5 M H₂SO₄ electrolyte, holding potential at 0.05 V for 30 min, followed by bubbling N₂ into the electrolyte for 30 min. CV was performed in the scan rate range of 10 to 100 mV/s to calculate the double-layer capacitance (C_{dl}). Subsequently, a LSV curve was recorded by scanning from 0.1 V to 1.05 V at a rate of 100mV/s. Accelerated durability test was performed between 0 V and -0.1 V versus RHE using CV at 100 mV/s in 0.5 M H₂SO₄ solution. The chronopotentiometry test was performed with a constant current density of -10 mA/cm². The turnover frequency (TOF) was calculated by the following equation: $TOF=i/nFN$, where i is the HER current, n is the electron transfer number of the reaction ($n = 2$ for HER), F is the Faraday constant, and N can be calculated by the following equation: $N=ECSA \times M \times N_0/N_A$, where M is the mass loading of Pt at the electrode, N_0 is the constant of Pt surface concentration (1.77×10^{15} atoms/cm² for Pt₂CoNi IMC and 1.64×10^{15} atoms/cm² for 20% Pt/C), and N_A is the Avogadro constant.

Electrochemical measurements of HOR. The ink was drop-coated on the glassy

carbon rotating disk as a working electrode (5mm inner diameter, 0.2475 cm²) with Pt loading of 6 ug/cm² and dried naturally. The activation was performed by CV at a scan rate of 200 mV/s for 20 cycles. LSV was then conducted in H₂-saturated 0.1 M HClO₄ by sweeping the potential from -0.03 V to 0.6 V at 5 mV/s (1600 rpm). 80% iR-correction were performed on all catalysts. Tafel slope was calculated with according to the polarization profiles. For the durability evaluation, the chronoamperometry were obtained under the constant potential of 0.1 V (vs. RHE) in H₂-saturated electrolyte. Kinetic current density (j^k) could be extracted from the Koutecky-Levich equation:

$$\frac{1}{j} = \frac{1}{j^k} + \frac{1}{j^d} = \frac{1}{j^k} + \frac{1}{Bc_0\omega^{1/2}}$$

where j , B , c_0 , and ω are the measured current density, the Levich constant, the solubility of H₂, and the speed of the rotating, respectively.

Exchange current density (j^0) could be extracted from the Butler-Volmer equation:

$$j^k = j^0 \times \left[e^{\frac{\alpha F}{RT}\eta} - e^{-\frac{(1-\alpha)F}{RT}\eta} \right]$$

where α , η , R , T , and F represent the transfer coefficient, the overpotential, the universal gas constant (8.314 J/(mol K)), the temperature (298 K), and the Faraday constant (96500 C/mol), respectively.

Calculation methods.

DFT calculations were performed using the Vienna ab initio simulation package (VASP). The electron-ion interaction was represented by using the projector-augmented wave (PAW) pseudopotentials.[1, 2] The electron exchange correlation interaction was described by using the Perdew-Burke-Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).[3] The plane-wave energy cutoff was taken as 400 eV and the Brillouin zone was sampled with a 3×3×1 k-point mesh according to the Monkhorst-Pack scheme.[4] The convergence criteria were set as 10⁻⁵ eV in energy and 0.01 eV/Å in force. The (5×2×1) supercell was built to represent the Pt (100) surface. The Pt₂CoNi IMC (100) surface was modeled based on experimental data, including five atomic layers of (2×1) supercell in two different crystal orientations. Co atoms and Ni atoms in IMC were randomly distributed by

special quasi-random supercell method (SQS).[5] All surface structural models had a vacuum region of more than 15 Å thickness. The free energy change (ΔG_{*H}) of reaction was defined by

$$\Delta G_{*H} = \Delta E_{*H} + \Delta ZPE - T\Delta S \quad (1)$$

$$\Delta E_{*H} = E_{\text{slab}+*H} - E_{*H} - E_{\text{ads}} \quad (2)$$

where ΔE_{*H} is the adsorption energy change of $*H$ at different models, ΔZPE is the zero-point energy change, ΔS is the entropy change, $E_{\text{slab}+*H}$ is the total energy of the adsorption system, E_{slab} is the total energy of the bare slab, and E_{*H} is the total energy of the adsorbate in a vacuum.

Supporting Figures and Tables.

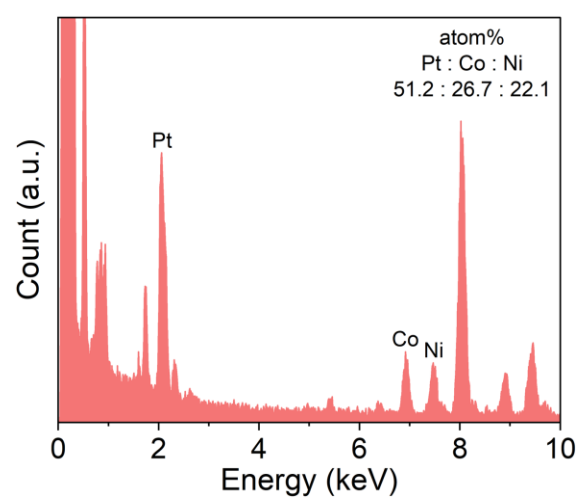


Figure S1. EDS spectrum of the Pt₂CoNi IMC nanocatalyst.

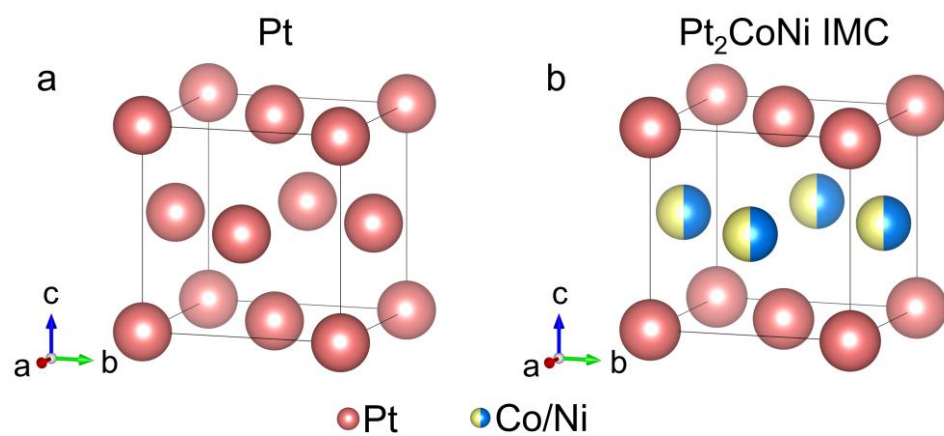


Figure S2. Unit cells of (a) Pt and (b) Pt₂CoNi IMC.

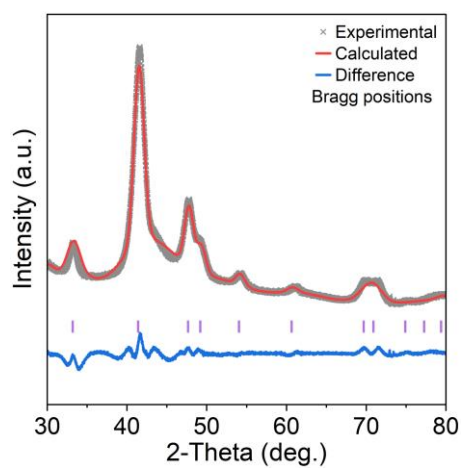


Figure S3. Rietveld refined XRD results for Pt₂CoNi IMC nanocatalyst. Experimental data, calculated profile, allowed Bragg diffraction positions, and difference curve are marked with cross, line, cyan vertical bars, and purple line, respectively.

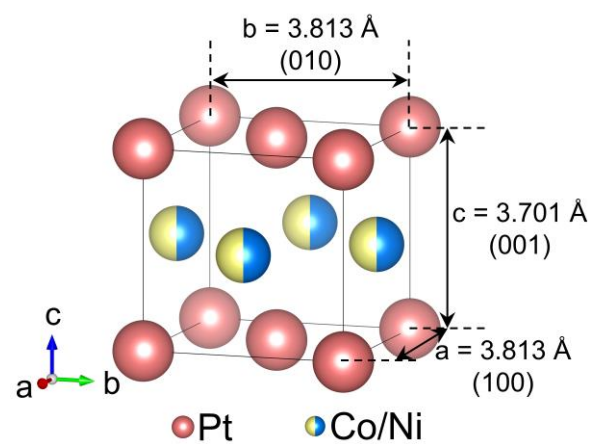


Figure S4. Lattice parameters of Pt₂CoNi IMC.

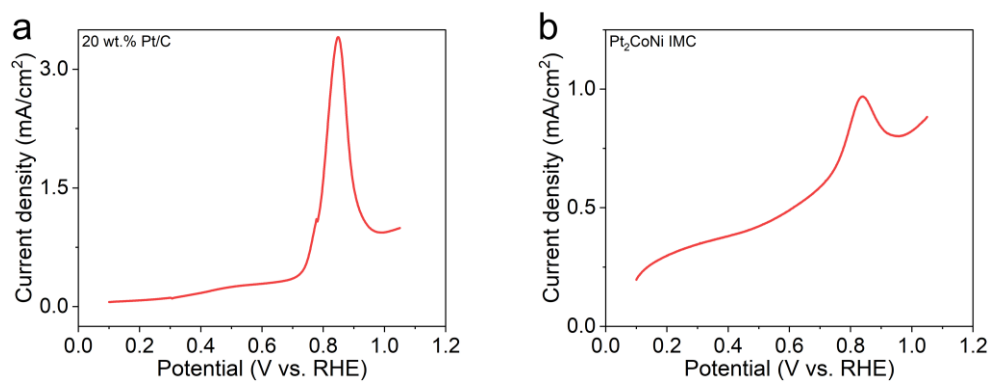


Figure S5. CO-stripping curves of (a) 20 wt.% Pt/C and (b) Pt₂CoNi IMC nanocatalyst.

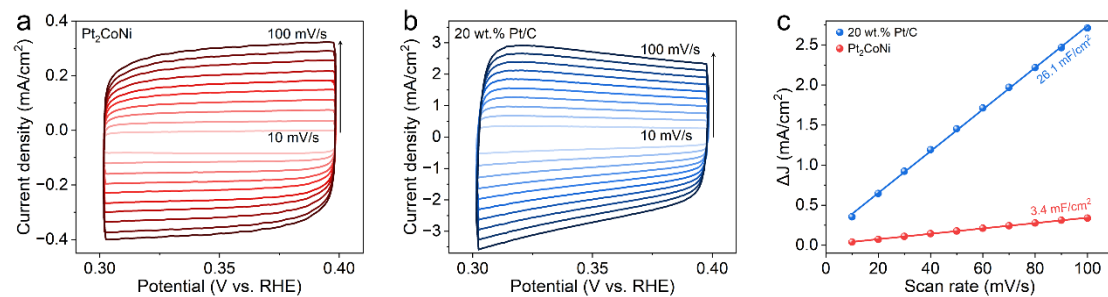


Figure S6. Double-layer capacitance measurements for (a) Pt₂CoNi IMC nanocatalyst and (b) 20 wt.% Pt/C. (c) C_{dl} plots for 20 wt.% Pt/C and Pt₂CoNi IMC nanocatalyst.

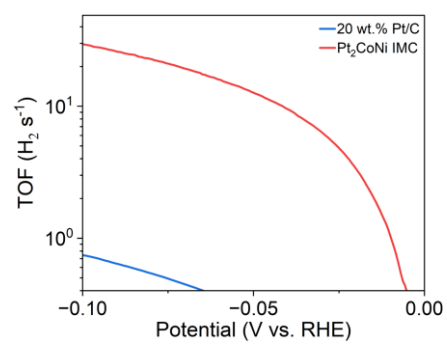


Figure S7. TOF values of 20 wt.% Pt/C and Pt_2CoNi IMC nanocatalyst.

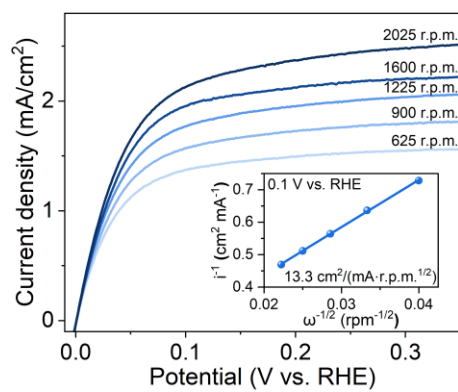


Figure S8. Polarization curves of 20 wt.% Pt/C in H₂-saturated 0.1 M HClO₄ at the rotation rates of 625, 900, 1225, 1600, and 2025 r.p.m., respectively. Inset shows the Koutecky-Levich plot at 0.1 V vs. RHE.

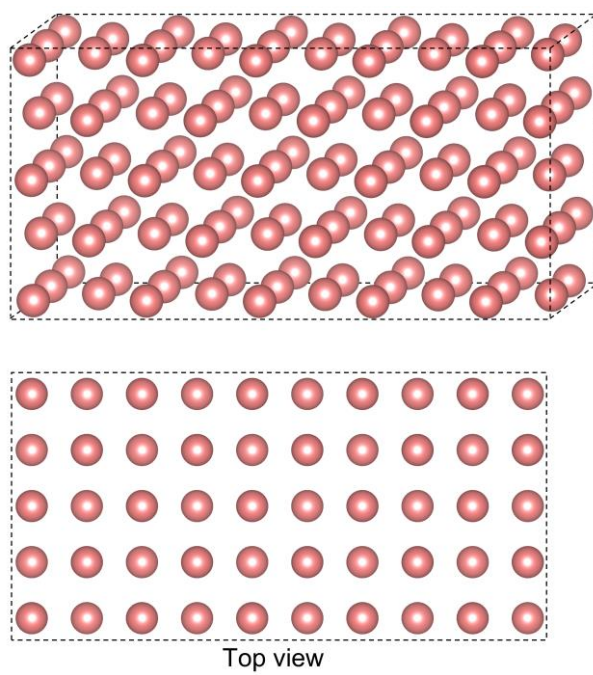


Figure S9. The Pt model for DFT calculation.

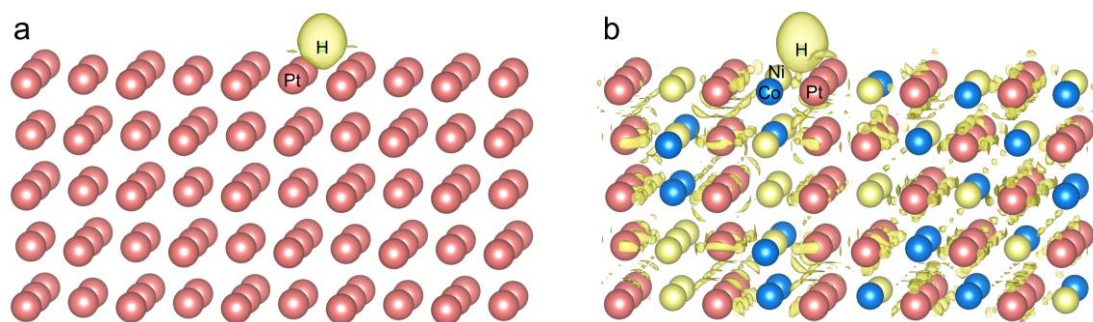


Figure S10. The ELF of (a) Pt model and (b) Pt₂CoNi IMC model with the adsorption of H atom. The isosurface value is 0.38 e/bohr³.

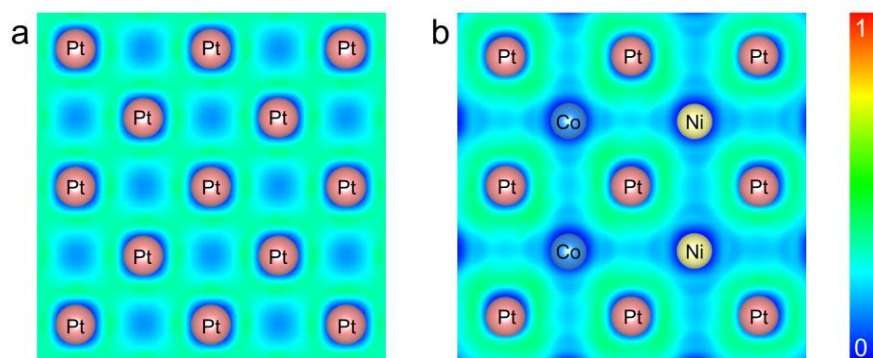


Figure S11. Sliced ELFs along the (0 0 1) direction for (a) Pt model and (b) Pt₂CoNi IMC model.

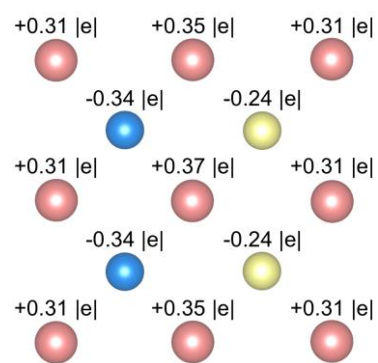


Figure S12. Bader charge analysis of atoms in Pt₂CoNi IMC model.

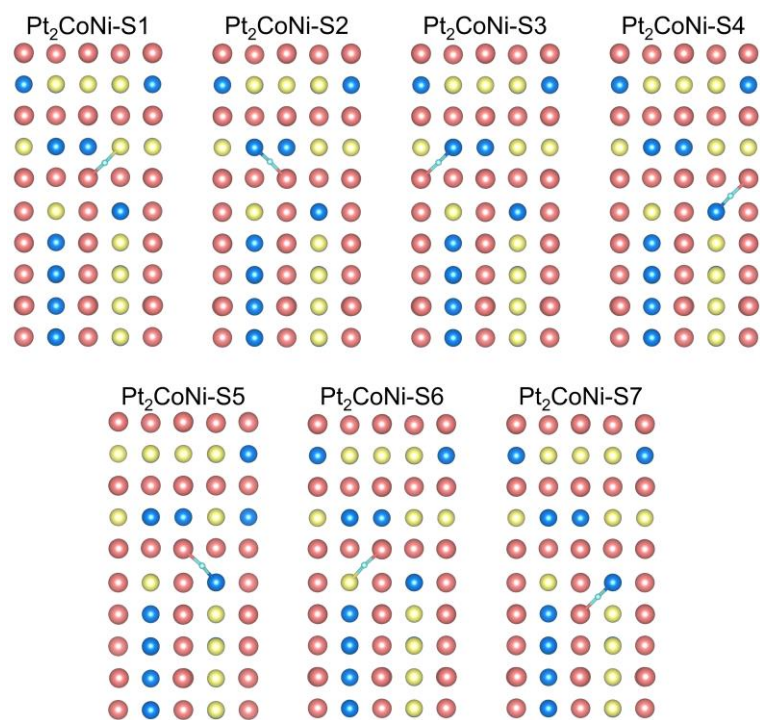


Figure S13. Adsorbed behavior of H for Pt_2CoNi IMC model on different surface active sites.

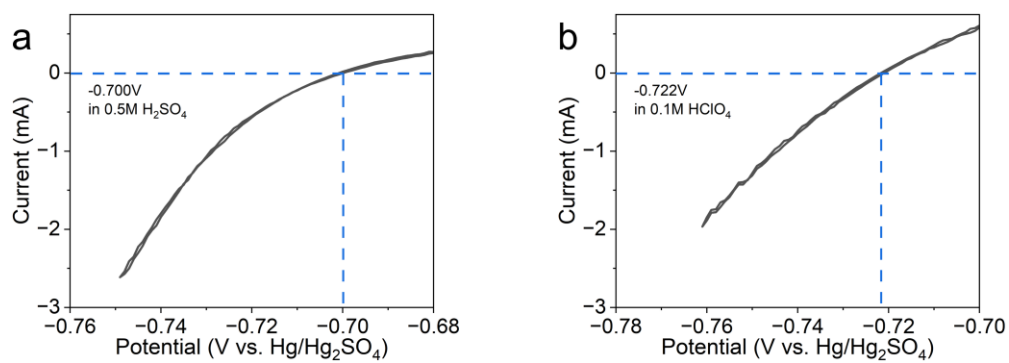


Figure S14. Calibration of Hg/HgSO₄ reference electrode to RHE in H₂-saturated (a) 0.5 M H₂SO₄ and (b) 0.1 M HClO₄.

Table S1. The weight percentage of Pt, Co, and Ni elements in the Pt₂CoNi IMC nanocatalyst from ICP-OES analysis.

Catalysts	Pt (wt.%)	Co (wt.%)	Ni (wt.%)
Pt ₂ CoNi IMC	4.8	0.7	0.7

Table S2. Structural information of the Pt₂CoNi IMC nanocatalyst.

Catalysts	Ordering degree ^a (%)	Particle size-XRD ^b (nm)	Particle size-STEM (nm)
Pt ₂ CoNi IMC	50	5.9	5.8

^a Ordering degree is calculated from $\frac{I_{110}/I_{111}}{I_{110}^*/I_{111}^*} \times 100\%$, in which I_{110} and I_{111} are the intensity of the superlattice (110) and foundational (111) diffraction peak, respectively, and I^* is the corresponding peak intensity of the fully ordered PtCo IMC structure.

^b Particle size-XRD is calculated from $\frac{K \times \gamma}{B \times \cos \theta}$, in which K is Scherrer constant (a value of 0.89), γ is X-ray wavelength (a value of 0.15406 for Cu $k\alpha$), B is full width at half maxima of the diffraction peak of (111) and θ is the diffraction angle of the diffraction peak of (111).

Table S3. Lattice parameters obtained from Rietveld refinement of the XRD for Pt₂CoNi IMC.

Catalysts	Cell parameters					R _{wp} (%)	χ^2
	Crystal system	Space group	a = b (Å)	c (Å)	V (Å ³)		
Pt ₂ CoNi IMC	Tetragonal	P4/mmm	3.813	3.701	56.806	3.81	4.21

Table S4. Electrolyte resistivity (R_s) and electron transfer resistivity (R_{ct}) fitted from EIS analysis of Pt₂CoNi IMC and 20 wt.% Pt/C in HER.

Catalysts	R_s (Ω)	R_{ct} (Ω)
Pt ₂ CoNi IMC	2.29	1.03
20 wt.% Pt/C	2.43	12.1

Table S5. Comparisons of η_{10} and MA at 0.05 V vs. RHE between Pt₂CoNi IMC and reported catalysts in HER.

Catalysts	η_{10} (mV)	MA (A/mg _{PGM})	Reference
Pt ₂ CoNi IMC	11.9	1.02	This work
Ir _{0.8} Rh _{0.2} Sb	39	0.055	[6]
Ru SNC/W ₁₈ O ₄₉	21	0.09	[7]
PtSi	22	0.11	[8]
IrSi	24	0.33	[9]
PtZnCo	20	0.465	[10]
Pt/N-CoWO ₃	20	0.082	[11]
Pt ₅₆ Fe ₄₄	48	0.084	[12]
PtCo@PtSn	21	0.014	[13]
PtCo	27	0.01	[13]
PtSn	32	0.005	[13]
RuGa/N-rGO	30	0.39	[14]
PtCu-MoO ₂ @C	42	0.49	[15]
PtW NPs/C	19.4	0.57	[16]
Pt/RuCeOx-PA	41	0.375	[17]

Table S6. Comparisons of the $j^{k, m}$ at 0.05 V vs. RHE between Pt₂CoNi IMC and reported catalysts in HOR.

Catalysts	$j^{k, m}$ (A/mg _{PtGM})	Reference
Pt ₂ CoNi IMC	4.08	This work
Pt-CeO _x	2.84	[18]
PtMo-CeO _x	2.33	[18]
Pt@Co-NC	2.21	[19]
PtMo	2.01	[18]
Co-IrRu/C	1.44	[20]
Ru/TiO _x /C	0.82	[21]
Ru NP/W ₁₈ O ₄₉	0.44	[7]
Pt/Ti ₃ C ₂ T _x -CNT	0.31	[22]
Ru@RuO ₂ /TiO ₂	0.22	[23]
Pd ₃ P/C	0.21	[24]

Table S7. The values of ΔG_{*H} on different structural configuration models.

Structural configuration models	ΔG_{*H} (eV)
Pt	-0.512
Pt ₂ CoNi-S1	-0.442
Pt ₂ CoNi-S2	-0.493
Pt ₂ CoNi-S3	-0.499
Pt ₂ CoNi-S4	-0.509
Pt ₂ CoNi-S5	-0.505
Pt ₂ CoNi-S6	-0.467
Pt ₂ CoNi-S7	-0.503

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