Electronic Supplementary Information

Experimental section

Materials: Cobaltous nitrate $(Co(NO_3)_2 \cdot 6H_2O)$, ammonium fluoride (NH_4F) , and urea $(CO(NH_2)_2)$ were purchased from Aladdin Ltd. (Shanghai, China). Pt/C (20wt% Pt) was bought from Sigma-Aldrich Chemical Reagent Co., Ltd. Ti mesh (TM) was provided by Suzhou Taili New Energy Co., Ltd. and cleaned by sequential sonication in acetone, ultrapure water and ethanol several times to remove the impurity. All the chemicals in the experiments were analytical grade and used without further treatments. Deionized water we used during the experiment process was purified through a Millipore system.

Preparation of CCH/TM, PtO₂–CCH/TM and PtCo–Co/TM: In a typical synthesis, $Co(NO_3)_2 \cdot 6H_2O$ (0.485 g), NH_4F (0.155 g) and urea (0.500 g) were dissolved in 33 mL of ultrapure water. The aqueous solution and the pretreated TM were transferred into a 40 mL Teflon-lined stainless autoclave, which was sealed and maintained at 120 °C for 6 h. Finally, as-made precursors were thoroughly washed with ultrapure water and dried to obtain CCH/TM. Then the CCH/TM was mixed with 30 mL H₂PtCl₆ aqueous solution (66.7 µg mL⁻¹) and transferred into a 40 mL Teflon-lined stainless autoclave, and hydrothermally treated at 120 °C for 4 h. Finally, the PtO₂–CCH/TM was thoroughly washed with ultrapure water, and dried to obtain CCH/TM was placed in an alumina boat and calcined at 400 °C for 2 h with 5 °C min⁻¹ under 5 wt% H₂/Ar flow and then cooled down to room temperature, obtaining PtCo–Co/TM.

Preparation of Pt/C doped TM: In brief, 10 mg commercial Pt/C and 20 μ L 5 wt% nafion solution were mixed in 1 mL water/ethanol solvent under sonication for 30 min. Then 18 μ L ink of Pt/C was loaded on TM with the catalyst loading of about 0.72 mg cm⁻² with an area of 0.25 cm⁻² (0.5 × 0.5 cm), and dried at 60 °C for 4 h.

Characterization: Powder X-ray diffraction (XRD) patterns were acquired on a RigakuD/MAX 2550 diffractometer with Cu K α radiation ($\lambda = 1.5418$ Å). Scanning electron microscopy (SEM) measurements were made on a Hitachi S-4800 field

emission scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscope (TEM) images were taken on a Hitachi H-8100 electron microscopy (Hitachi, Tokyo, Japan) at an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALABMK II X-ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurement: Electrochemical measurements were performed with a CHI660E potentiostat (CH Instruments, China) in a standard three-electrode setup, in which as-synthesized material as the working electrode, a graphite rod as the counter electrode and the Hg/HgO as the reference electrode. In all measurements, reference electrode was calibrated with respect to reversible hydrogen electrode (RHE), E (RHE) = E (Hg/HgO) + 0.059 pH + 0.098 V. LSV curves were obtained using linear sweep voltammetry (LSV) curves conducted in alkaline media with a scan rate of 5 mV s⁻¹. All experiments were carried out at 25 °C.

Faradaic efficiency (FE) determination: The generated gas was confirmed by gas chromatography (GC) analysis and measured quantitatively using a calibrated pressure sensor to monitor the pressure change in the cathode compartment of a H-type electrolytic cell. The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic anodic electrolysis with calculated H₂ (assuming 100% FE). The theoretical hydrogen is calculated from the total charge during the electrolysis:

$$n_{\rm H2} = Q/2F \tag{1}$$

where n_{H2} (mol) is the mole of theoretical H₂, *F* (96485 C mol⁻¹) is the Faraday constant, 2 is denoted as two electrons needed to produce one H₂ molecule, and *Q* (C) is the electric quantity during the electrolysis. GC analysis was carried out on GC–2014C (Shimadzu Co.) with thermal conductivity detector and nitrogen carrier gas. Pressure data during electrolysis were recorded using a CEM DT-8890 differential air pressure gauge manometer data logger meter tester with a sampling interval of 1 point per second. The cell geometry and the working electrode connections was shown in Scheme S1.



Scheme S1. The construction of H-type three-electrode cell and the working electrode connections

Computational details: Spin polarized calculations were carried out within the density functional theory (DFT) framework embedded in the Vienna Ab initio Simulation Package (VASP).^{1–3} The projector augmented-wave (PAW) technique^{4,5} was used, and the plane-wave energy cutoff was set to 400 eV. The Perdew-Burke-Ernzerhof (PBE) functional was applied to treat the correlation-exchange energies of all systems.⁶ The sampling over Brillouin zone was treated by a ($3 \times 3 \times 1$) Monkhorst-Pack grid. During the geometry optimization process, the total energy tolerance was set to 10^{-5} eV and the force on the atoms was set to 0.02 eV Å^{-1.7} The simulations were performed based on a Pt (111) slab model, a Co (111) slab model, and a Co termination of PtCo (100) slab model and Pt termination PtCo (100) slab model, and a vacuum of 15 Å was considered to all slabs to avoid the pseudo interactions between the periodic images along z axis.

Gibbs free energy is usually employed as a key descriptor in predicting theoretical activity for hydrogen evolution reaction. The free energy diagram for HER was obtained by calculating the change of the free energy with a hydrogen atom adsorbed on the surface following the computational hydrogen electrode model. The Gibbs free energy of a single H atom on different surfaces ($\Delta G_{\text{H}*}$) was calculated by the following equation:⁷

$$\Delta G_{\mathrm{H}*} = \Delta E_{\mathrm{H}*} + \Delta E_{\mathrm{ZPE}} - T\Delta S \qquad (2)$$

where $\Delta E_{\text{H*}}$ is the adsorption energy of H species. ΔE_{ZPE} and $T\Delta S$ are the changes of zero point energy (ZPE) and entropy (*S*), respectively. T represents the temperature of systems and is set to 298.15 K. The ΔE_{ZPE} and ΔS can be calculated by the following equations:

$$\Delta E_{\text{ZPE}} = \Delta E_{\text{ZPE}-\text{H}^*} - 1/2\Delta E_{\text{ZPE}-\text{H}2} \qquad (3)$$

$$\Delta S = \Delta S_{\mathrm{H}^*} - \Delta S_{\mathrm{H}^2} \tag{4}$$



Fig. S1 XRD patterns of CCH and PtO₂–CCH scratched from TM.



Fig. S2 SEM images of PtO₂–CCH/TM.



Fig. S3 HRTEM image of CCH.



Fig. S4 HRTEM images of PtO₂–CCH.



Fig. S5 HRTEM image of PtCo-Co.



Fig. S6 The EDX mapping images of PtCo-Co/TM.



Fig. S7 XPS spectrum of Co 2p for PtCo-Co/TM.



Fig. S8 CVs of (a) PtO_2 -CCH/TM and (b) PtCo-Co/TM with various scan rates (5-100 mV s⁻¹) in the region of -0.1 to 0 V.



Fig. S9 HRTEM image of PtCo-Co after stability test.

		η at 10 mA cm ⁻²		<i>i</i> at 0.07 V			
Samples	Pt loading	(m	V)	(mA	cm ⁻²)	References	
Sumples	$(mg cm^{-2})$	0.1 M	1.0 M	0.1 M	1.0 M		
		КОН	КОН	КОН	KOH		
PtCo-Co/TM	0.043		28		46.5	This work	
Ni ₃ N/Pt	~0.3	—	50		~35	8	
hcp-Pt-Ni	0.008	~67		~24.2	—	9	
Pt ₃ Ni ₂ NWs-S/C	0.015	45	42	20.2	37.2	10	
Zn _{0.30} Co _{2.70} S ₄ nanocrystals	0.285	_	85	_	~7	11	
MoC _x	0.8	—	~151		~0	12	
Pt NWs/ SL-Ni(OH) ₂	0.016	~48	~70	26.6	10.9	13	
Ni _{0.33} Co _{0.67} S ₂ NWs/Ti foil	0.3	_	88	—	~7	14	
Ni ₃ S ₂ /Ni foam	1.6	_	223	_	~1.5	15	
CeO ₂ /Ni-CNT	0.14	—	~91		~7.5	16	
Mo ₂ C@NC	0.28	_	~60		~12	17	
NiO/Ni-CNT	0.28	_	~80		~8.5	18	
CoP/carbon cloth	0.92	_	~250		~0	19	
MoP	0.86	_	~140	_	~0	20	
Ni(OH) ₂ modified Pt	—	~75	_	~9.5	_	21	
CoP films	2.71	—	~94	—	~5	22	
Ni(OH) ₂ /Pt(111) surface	_	~138	_	~2.2	_	23	

Table S1 Comparison of HER activity of PtCo-Co/TM with other high-performance

 catalysts reported in recent literatures under similar conditions.

Species	ΔE_{H^*}	$E_{\rm ZPE}$	<i>-TS</i>	ΔG_{H^*}
H_2	_	0.273	-0.410	_
H on Pt (111) surface	-0.374	0.192	_	-0.134
H on Co (111) surface	-0.505	0.119	_	-0.265
H on Co termination of PtCo	-0.256	0.177	_	-0.011
H on Pt termination of PtCo	-0.296	0.157	_	-0.071

Table S2 Adsorption energy of H species (ΔE_{H^*} , eV), E_{ZPE} (eV), and -*TS* (eV) for different systems.

References

- 1 G. Kresse and J. Furthmüller, Comp. Mater. Sci., 1996, 6, 15–50.
- 2 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14269.
- 3 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 4 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 5 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 6 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 7 J. S. Li, Y. Wang, C. H. Liu, S. L. Li, Y. G. Wang, L. Z. Dong, Z. H. Dai, Y. F. Li and Y. Q. Lan, *Nat. Commun.*, 2016, 7, 11204.
- Y. Wang, L. Chen, X. Yu, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2017, 7, 1601390.
- 9 Z. Cao, Q. Chen, J. Zhang, H. Li, Y. Jiang, S. Shen, G. Fu, B.-a. Lu, Z. Xie and L. Zheng, *Nat. Commun.*, 2017, 8, 15131.
- 10 P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nat. Commun.*, 2017, 8, 14580.
- J. Yin, Q. Fan, Y. Li, F. Cheng, P. Zhou, P. Xi and S. Sun, J. Am. Chem. Soc.,
 2016, 138, 14546–14549.
- H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu and X. W. Lou, *Nat. Commun.*, 2015, 6, 6512.
- H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, 6, 6430.
- 14 Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, *Adv. Energy Mater.*, 2015, 5, 1402031.
- 15 L.-L. Feng, G. Yu, Y. Wu, G.-D. Li, H. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, J, Am. Chem. Soc., 2015, 137, 14023–14026.
- 16 Z. Weng, W. Liu, L.-C. Yin, R. Fang, M. Li, E. I. Altman, Q. Fan, F. Li, H.-M. Cheng and H. Wang, *Nano Lett.*, 2015, **15**, 7704–7710.
- 17 Y. Liu, G. Yu, G.-D. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, Angew. Chem., Int. Ed., 2015, 54, 10752–10757.

- M. Gong, W. Zhou, M. C. Tsai, J. Zhou, M. Guan, M. C. Lin, B. Zhang, Y. Hu, D.
 Y. Wang, J. Yang, S. J. Pennycook, B. J. Hwang and H. Dai, *Nat. Commun.*, 2014, 5, 4695.
- J. Tian, Q. Liu, A. M. Asiri and X. Sun, J. Am. Chem. Soc., 2014, 136, 7587– 7590.
- 20 P. Xiao, M. A. Sk, L. Thia, X. Ge, R. J. Lim, J.-Y. Wang, K. H. Lim and X. Wang, *Energy Environ. Sci.*, 2014, 7, 2624–2629.
- 21 N. Danilovic, R. Subbaraman, D. Strmenik, K.-C. Chang, A. P. Paulikas, V. R. Stamenkovic and N. M. Markovic, *Angew. Chem., Int. Ed.*, 2012, **51**, 12495–12498.
- N. Jiang, B. You, M. Sheng and Y. Sun, *Angew. Chem., Int. Ed.*, 2015, 54, 6251–6254.
- R. Subbaraman, D. Tripkovic, D. Strmenik, K.-C. Chang, M. Uchimura, A. P.
 Paulikas, V. Stamenkovic and N. M. Markovic, *Science*, 2011, 334, 1256–1260.