

Electronic Supplementary Information

Experimental Section

Materials: Cobaltous nitrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$), chloroplatinic acid hexahydrate ($\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$) and potassium hydroxide (KOH) were purchased from Aladdin Ltd. (Shanghai, China). Ti mesh (TM) was provided by Suzhou Taili New Energy Co., Ltd. All the chemicals and solvents in the experiments were analytical grade and used without further treatments.

Preparation of $\alpha\text{-Co}(\text{OH})_2$ nanosheet on TM ($\text{Co}(\text{OH})_2/\text{TM}$): Ti mesh possesses negligible HER activity, favorable electronic conductivity, open structure allowing solvent good access at the reaction interface, and easy adhesion of the materials. Thus, we chose the Ti mesh as a substrate to support active materials in this work. Before electrodeposition, Ti mesh was washed with HCl, ethanol, and water for several times with sonication. The electrodeposition was performed in 0.05 M $\text{Co}(\text{NO}_3)_2$ using a three-electrode cell by a CHI 660E electrochemical workstation at room temperature. The cleaned Ti mesh (1×4 cm) was used as the working electrode, and a graphite rod and saturated calomel electrode (SCE) were used as the counter electrode and reference electrode, respectively. The electrodeposition was performed by cyclic voltammetry (CV) within the potential windows from -1.2 to -0.8 V vs. SCE with a scan rate of 50 mV s^{-1} . After deposition for 50 cycles, the as-prepared $\text{Co}(\text{OH})_2/\text{TM}$ was rinsed and then dried at 60 °C for 12 h.

Preparation of PtO_2 anchored $\text{Co}(\text{OH})_2$ nanosheet on TM ($\text{PtO}_2\text{-Co}(\text{OH})_2/\text{TM}$): For a typical procedure, the $\text{Co}(\text{OH})_2/\text{TM}$ was mixed with 30 mL water containing 20 μL of H_2PtCl_6 aqueous solution (0.1 g mL^{-1}). And then they were transferred into a 40 mL Teflon-lined stainless autoclave, and hydrothermally treated at 120 °C for 4 h. Finally, the $\text{PtO}_2\text{-Co}(\text{OH})_2/\text{TM}$ was thoroughly washed with water and dried at 60 °C overnight.

Preparation of PtO_2 anchored amorphous CoOOH nanosheet on TM ($\text{PtO}_2\text{-CoOOH}/\text{TM}$): To obtain $\text{PtO}_2\text{-CoOOH}/\text{TM}$, the $\text{PtO}_2\text{-Co}(\text{OH})_2/\text{TM}$ as the working electrode was conducted by cyclic voltammetry in 1.0 M KOH, using the graphite rod as the counter electrode and SCE as the reference electrode. For comparison, as-prepared $\text{Co}(\text{OH})_2/\text{TM}$ was also anodized at the same conditions to synthesize CoOOH/TM .

Preparation of the electrode for as-synthesized PtO_2 loaded on TM (PtO_2/TM): For large-scale synthesis of PtO_2 , 1 g of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ was dissolved in 30 mL of ultrapure water, then the solution was transferred into a 40 mL Teflon-lined stainless autoclave, which was sealed at 180 °C for 24 h. After cooled down to ambient temperature, the PtO_2 was collected by centrifugation and washed with water. To fabricate PtO_2 electrode, 20 mg of PtO_2 and 20 μL of Nafion solution (5 wt%) were

dispersed in 1 mL water/ethanol solvent (v:v = 1:1) with sonication for 30 min. Then 13 μL catalyst ink was loaded on bare Ti mesh (0.5×0.5 cm) with a catalyst loading of about 1.05 mg cm^{-2} .

Preparation of the electrode for commercial Pt/C loaded on TM: To prepare commercial Pt/C electrodes, 20 mg of commercial Pt/C (20 wt% Pt) and 20 μL of 5 wt% Nafion solution were dispersed in 1 mL water/ethanol solvent (v:v = 1:1) with sonication for 30 min. Then 13 μL catalyst ink was loaded on bare Ti mesh (0.5×0.5 cm) with a catalyst loading of 1.05 mg cm^{-2} .

Characterizations: X-ray diffraction patterns were performed using a LabX XRD-6100 X-ray diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) at 40 kV and 40 mA. Scanning electron microscopy (SEM) images were collected on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The elemental mapping was carried out on a field-emission scanning electron microscope (Hitachi S4800) equipped with an energy dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) images were made on a HITACHI H-8100 electron microscopy with 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. Elemental analysis was performed to determine actual weight loading of Co and Pt by the inductively coupled plasma atomic emission spectroscopy.

Electrochemical measurements: Electrochemical measurements were performed in a standard three-electrode setup by a CHI 660E electrochemical workstation, using the $\text{PtO}_2\text{-CoOOH/TM}$, a graphite rod and Hg/HgO electrode as the working electrode, the counter electrode and the reference electrode, respectively. All the potentials of the electrodes should be made the iR correction by measuring the uncompensated Ohmic resistance for each electrode in the electrolyte solution, which were recorded on RHE using the following equation: $E (\text{RHE}, \text{V}) = E (\text{Hg/HgO}) + 0.059 \times \text{pH} + 0.098 - iR$. Prior to the electrochemical testing, the KOH solutions were purged with nitrogen for 30 min. Polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s^{-1} . The long-term durability test was performed using chronopotentiometric measurements. Multi-current steps of electrodes were conducted at the current densities between 20 and 200 mA cm^{-2} with an increment of 20 mA cm^{-2} per 500 s. All experiments were carried out at $25 \text{ }^\circ\text{C}$.

Faradaic efficiency (FE) determination: The FE was calculated by comparing the amount of hydrogen generated by potentiostatic cathode electrolysis at -0.05 V with calculated hydrogen amount. The generated hydrogen during electrolysis was recorded on a CEM DT-8890 Differential Air Pressure Gauge Manometer Data Logger Meter Tester with a sampling interval of one point per

second.

Computational details: Spin-polarized density functional theory (SP-DFT) calculations were performed using the Vienna ab initio simulation package (VASP).¹⁻³ We employed the Perdew-Burke-Ernzerhof (PBE) function for the calculation of the exchange-correlation energy⁴ and projector augmented wave (PAW) potentials.^{5,6} The kinetic energy cutoff was set to 450 eV, and the ionic relaxation was carried out until the force on each atom is less than 0.02 eV Å⁻¹. The k-point mesh was 3×3×1 using Monkhorst-Pack method.⁷ The simulations were performed based on a PtO₂(111) slab model, a CoOOH(111) slab model and interface of PtO₂ and CoOOH with one PtO₂ unit on the CoOOH(111) substrate. To minimize the undesired interactions between images, a vacuum of at least 10 Å was considered along the z axis. The climbing image nudged elastic band (cNEB)⁸ method was used to examine the energy profiles along selected pathways for H₂O dissociation.

The free energy change for H* adsorption (ΔG_{H^*}) on catalyst surfaces was calculated as follows, which is proposed by Norskov and coworkers:⁹

$$\Delta G_{H^*} = E_{\text{total}} - E_{\text{sur}} - E_{\text{H}}^2/2 + \Delta E_{\text{ZPE}} - T\Delta S \quad (1)$$

where E_{total} is the total energy for the adsorption state, E_{sur} is the energy of pure surface, E_{H}^2 is the energy of hydrogen gases, ΔE_{ZPE} is the zero-point energy change and ΔS is the entropy change.

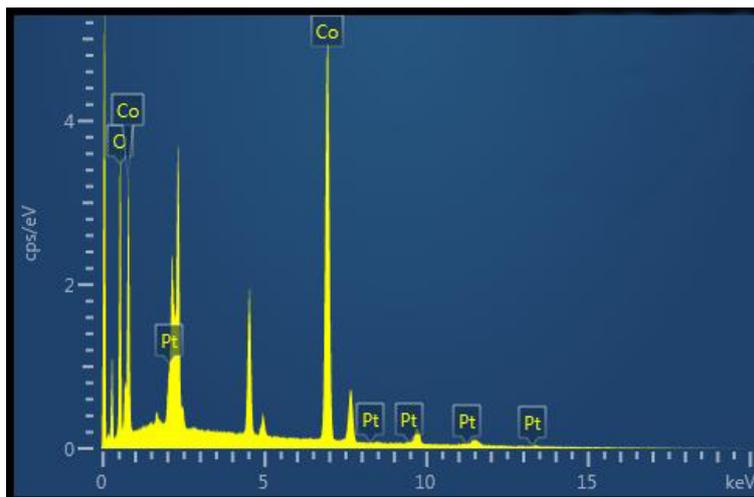


Fig. S1 EDX spectrum of the PtO₂-CoOOH/TM.

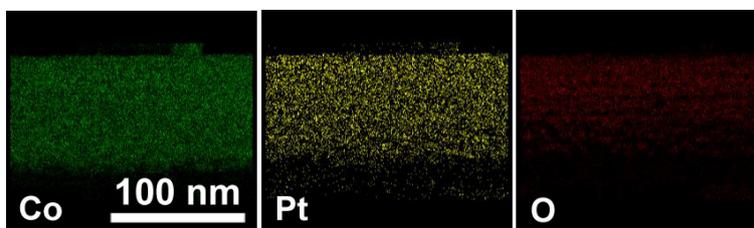


Fig. S2 EDX elemental mapping images of the PtO₂-CoOOH/TM.

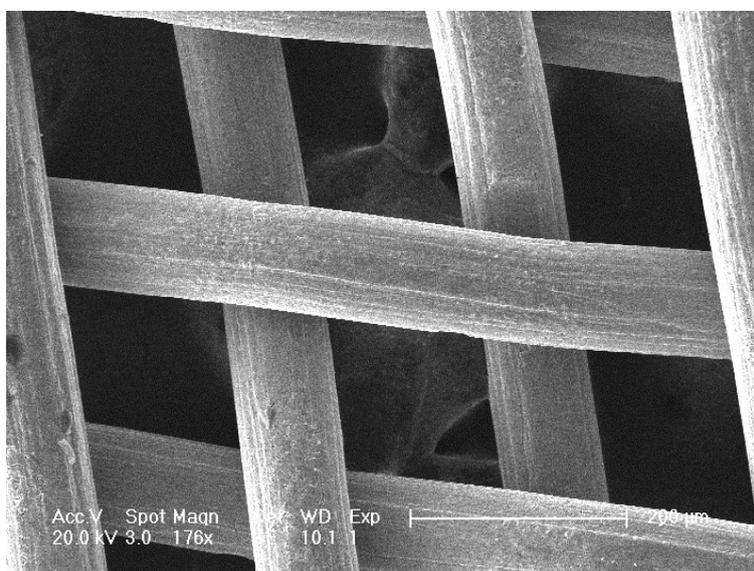


Fig. S3 SEM image of the bare TM.

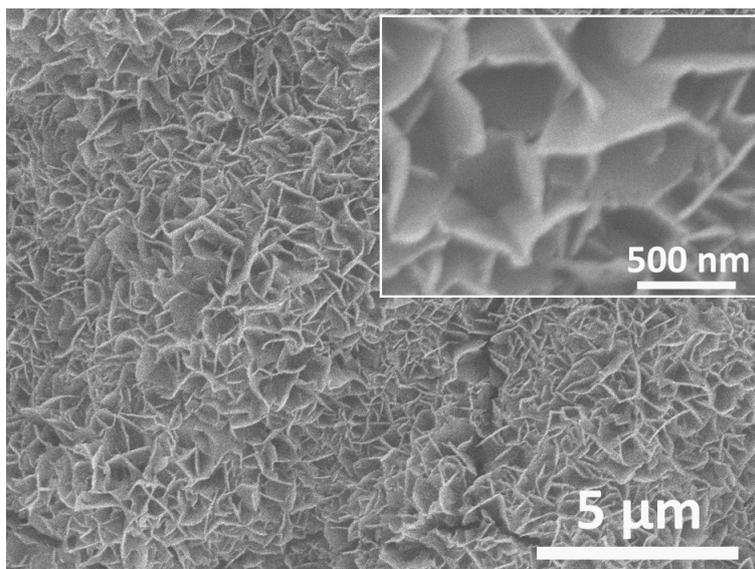


Fig. S4 SEM images of the PtO₂-Co(OH)₂/TM.

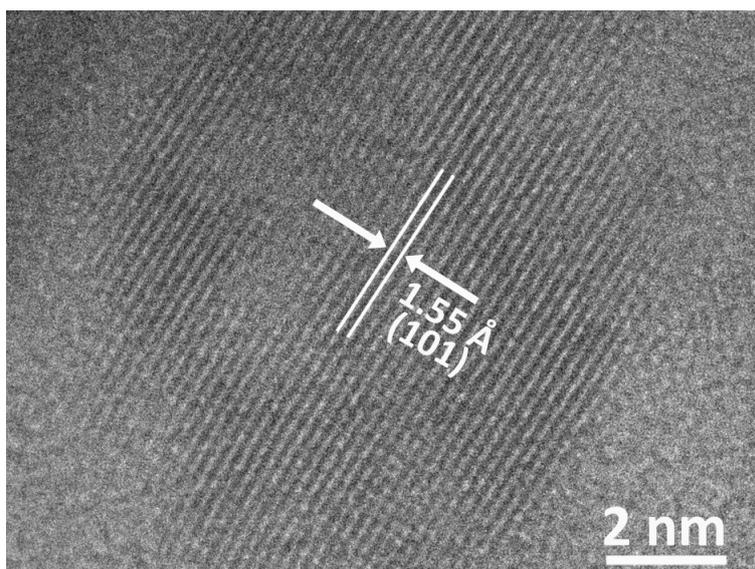


Fig. S5 High-resolution TEM image of the α-Co(OH)₂.

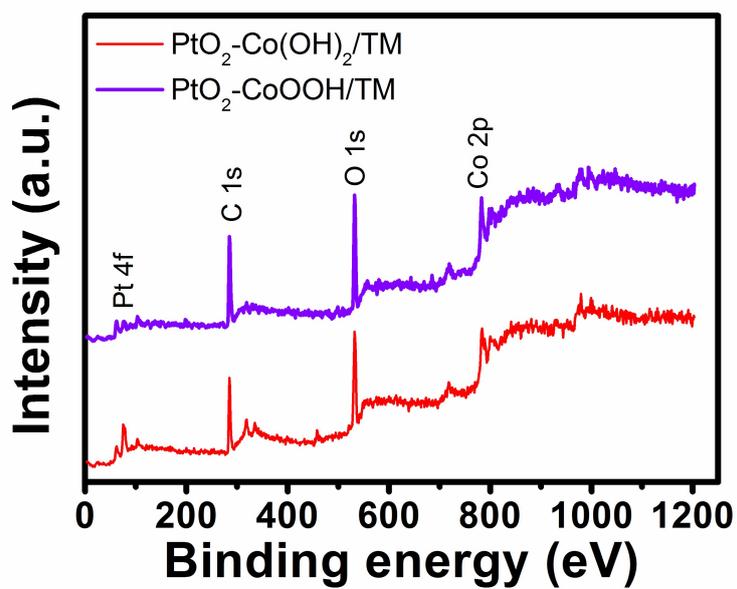


Fig. S6 The XPS survey patterns of the samples.

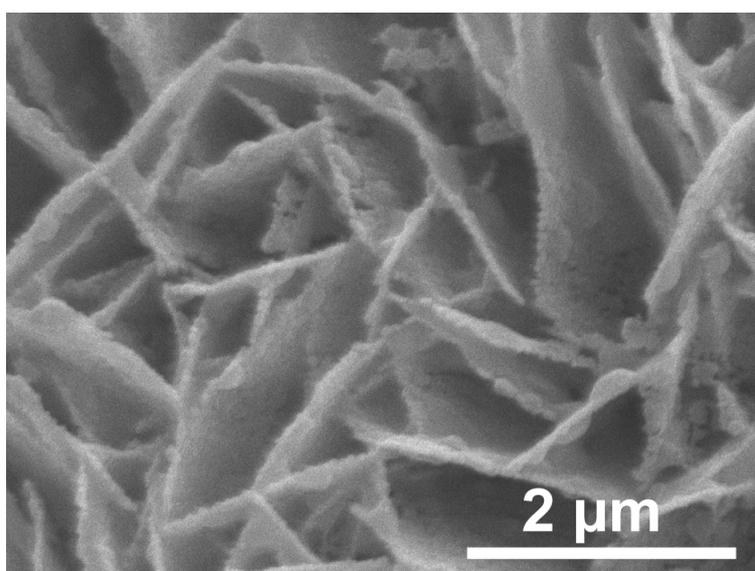


Fig. S7 SEM image of the PtO₂-CoOOH/TM after 1000 cycles.

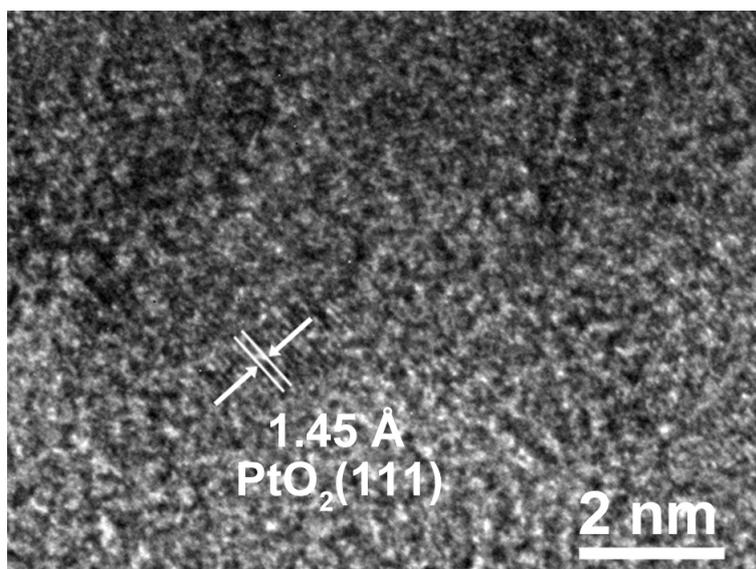


Fig. S8 HRTEM image of the PtO₂-CoOOH after long-term durability test.

Table S1 Comparison of HER performance of PtO₂-CoOOH/TM with recently reported catalysts.

Samples	Loading ^a (mg cm ⁻²)	η at 10 mA cm ⁻² (mV)		j at 70 mV (mA cm ⁻²)		References
		0.1 M KOH	1.0 M KOH	0.1 M KOH	1.0 M KOH	
PtO ₂ -CoOOH/TM	0.043(Pt)	—	14	—	65.1	This work
Ni ₃ N/Pt	~0.3(Pt)	—	50	—	~35	10
<i>hcp</i> -Pt-Ni	0.008(Pt)	~67	—	~24.2	—	11
Pt ₃ Ni ₂ NWS-S/C	0.015(Pt)	45	42	20.2	37.2	12
Zn _{0.30} Co _{0.70} S ₄ nanocrystals	0.285	—	85	—	~7	13
MoC _x	0.8	—	~151	—	~0	14
Pt NWS/SL-Ni(OH) ₂	0.016(Pt)	~48	~70	26.6	10.9	15
Ni _{0.33} Co _{0.67} S ₂ NWS/Ti foil	0.3(cat.)	—	88	—	~7	16
NiS nanoframes	2(cat.)	—	~94	—	~7	17
Ni ₃ S ₂ /Ni foam	1.6(cat.)	—	223	—	~1.5	18
Ni ₅ P ₄ /Ni films	—	—	~150	—	~0	19
CeO ₂ /Ni-CNT	0.14(cat.)	—	~91	—	~7.5	20
Mo ₂ C@NC	0.28(cat.)	—	~60	—	~12	21
NiO/Ni-CNT	0.28(cat.)	—	~80	—	~8.5	22
CoP/Carbon Cloth	0.92(cat.)	—	~250	—	~0	23
MoP	0.86(cat.)	—	~140	—	~0	24
Ni(OH) ₂ modified Pt surface	Pt electrode	~75	—	~9.5	—	25
Ni(OH) ₂ /Pt -islands/Pt(111) surface	Pt electrode	~138	—	~2.2	—	26

^aThe Pt in the brackets is the Pt loading of the Pt-based catalysts, and the cat. in the brackets is the whole catalyst loading of Pt-free catalysts.

References

- 1 G. Kresse and J. Hafner, *Phys. Rev. B*, 1994, **49**, 14251–14269.
- 2 G. Kresse and J. Furthmüller, *Comp. Mater. Sci.*, 1996, **6**, 15–50.
- 3 G. Kresse and J. Furthmüller, *Phys. Rev. B*, 1996, **54**, 11169–11186.
- 4 J. P. Perdew, K. Burke and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865–3868.
- 5 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953–17979.
- 6 G. Kresse and D. Joubert, *Phys. Rev. B*, 1999, **59**, 1758–1775.
- 7 H. J. Monkhorst and J. D. Pack, *Phys. Rev. B*, 1976, **13**, 5188–5192.
- 8 G. Henkelman, B. P. Uberuaga and H. Jonsson, *J. Chem. Phys.*, 2000, **113**, 9901–9904.
- 9 J. K. Norskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen, S. Pandelov and J. K. Norskov, *J. Electrochem. Soc.*, 2005, **152**, J23–J26.
- 10 Y. Wang, L. Chen, X. Yu, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2017, **7**, 1601390.
- 11 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.
- 12 P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nat. Commun.*, 2017, **8**, 14580.
- 13 Z.-F. Huang, J. Song, K. Li, M. Tahir, Y.-T. Wang, L. Pan, L. Wang, X. Zhang and J.-J. Zou, *J. Am. Chem. Soc.*, 2016, **138**, 1359–1365.
- 14 H. B. Wu, B. Y. Xia, L. Yu, X.-Y. Yu and X. W. Lou, *Nat. Commun.* 2015, **6**, 6512.
- 15 H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, **6**, 6430.
- 16 Z. Peng, D. Jia, A. M. Al-Enizi, A. A. Elzatahry and G. Zheng, *Adv. Energy Mater.*, 2015, **5**, 1402031.
- 17 X.-Y. Yu, L. Yu, H. B. Wu and X. W. Lou, *Angew. Chem.*, 2015, **127**, 5421–5425.
- 18 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.
- 19 M. Ledendecker, S. K. Calderón, C. Papp, H.-P. Steinrück, M. Antonietti and M. Shalom, *Angew. Chem.*, 2015, **127**, 12538–12542.
- 20 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.
- 21 Y. Liu, G. Yu, G.-D. Li, Y. Sun, T. Asefa, W. Chen and X. Zou, *Angew. Chem., Int. Ed.*, 2015, **54**, 10752–10757.
- 22 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.
- 23 J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587–7590.
- 24 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.
- 25 N. Danilovic, R. Subbaraman, D. Strmcnik, K.-C. Chang, A. P. Paulikas, V. R. Stamenkovic and N. M. Markovic, *Angew. Chem., Int. Ed.*, 2012, **51**, 12495–12498.
- 26 R. Subbaraman, D. Tripkovic, D. Strmcnik, K.-C. Chang, M. Uchimura, A. P. Paulikas, V. Stamenkovic and N. M. Markovic, *Science*, 2011, **334**, 1256–1260.