Electronic Supplementary Material (ESI) for Chemical Communications. This journal is © The Royal Society of Chemistry 2018

## **Electronic Supplementary Information**

## **Experimental section**

**Materials:** Cobaltous nitrate hexahydrate (Co(NO<sub>3</sub>)<sub>2</sub> 6H<sub>2</sub>O), ammonium fluoride (NH<sub>4</sub>F), urea (CO(NH<sub>2</sub>)<sub>2</sub>), and and chloroplatinic acid hexahydrate (H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>O) were purchased from Aladdin Ltd. (Shanghai, China). 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. Ti mesh was chosen as the substrate for its negligible HER activity, acceptable electronic conductivity, open structure allowing solvent good access at the reaction interface and its ability to facilitate adhesion of the materials. All the chemicals in the experiments were analytical grade and used without further treatments.

**Preparation of Co(OH)F nanowire array on TM (Co(OH)F NA/TM):** In a typical synthesis,  $Co(NO_3)_2 \ 6H_2O \ (0.485 \text{ g})$ ,  $NH_4F \ (0.155 \text{ g})$  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 were sealed and maintained at 120 °C for 6 h. Finally, the Co(OH)F NA/TM was thoroughly washed with ultrapure water, and dried at 60 °C overnight.

**Preparation of PtO<sub>2</sub> anchored Co(OH)F nanowire array on TM (PtO<sub>2</sub>–Co(OH)F NA/TM):** For a typical procedure, the Co(OH)F NA/TM was mixed with 30 mL of H<sub>2</sub>PtCl<sub>6</sub> aqueous solution (66.7  $\mu$ g mL<sup>-1</sup>). And then they were transferred into a 40 mL Teflon-lined stainless autoclave, and hydrothermally treated at 120 °C for 4 h. Finally, the PtO<sub>2</sub>–Co(OH)F NA/TM was thoroughly washed with ultrapure water, and dried at 60 °C overnight.

**Preparation of the electrode for as-synthesized PtO<sub>2</sub> loaded on TM (PtO<sub>2</sub>/TM):** For the large-scale preparation of PtO<sub>2</sub>, 1 g of H<sub>2</sub>PtCl<sub>6</sub> 6H<sub>2</sub>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<sub>2</sub> was collected by centrifugation and washed with ultrapure water. To fabricate PtO<sub>2</sub> electrode, 30 mg of PtO<sub>2</sub> and 10  $\mu$ L of Nafion solution (5 wt%) were dispersed in 1 mL water/ethanol solvent (v:v = 1:1) with sonication for 30 min. Then 11  $\mu$ L of catalyst ink was loaded on bare Ti mash with a catalyst loading of 1.32 mg cm<sup>-2</sup>.

**Preparation of the electrode for commercial Pt/C loaded on TM:** To prepare commercial Pt/C electrodes, 30 mg of commercial Pt/C (20wt% Pt) and 10  $\mu$ L of Nafion solution (5 wt%) were dispersed in 1 mL water/ethanol solvent (v:v = 1:1) with sonication for 30 min. Then 11  $\mu$ L of catalyst ink was loaded on bare Ti mesh with a catalyst loading of 1.32 mg cm<sup>-2</sup>.

**Characterizations:** X-ray diffraction (XRD) patterns were performed using a LabX XRD-6100 X-ray diffractometer (SHIMADZU, Japan) with Cu K $\alpha$  radiation ( $\lambda = 1.5418$  Å) at 40 kV and 40 mA. Scanning electron microscopy (SEM) image was 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 (FESEM, Hitachi S4800) equipped with an energy dispersive X-ray spectrometer (EDX). Transmission electron microscopy (TEM) image was made on a HITACHI H-8100 electron microscopy with an accelerating voltage of 200 kV. X-ray photoelectron spectroscopy (XPS) measurement was 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 (ICP–AES).

**Electrochemical measurements:** Electrochemical measurements were performed by a CHI 660E electrochemical analyzer (CH Instruments, Inc.) with a standard three-electrode system using PtO<sub>2</sub>–Co(OH)F NA/TM as the working electrode, graphite plate as the counter electrode and Hg/HgO as the reference electrode. All potentials measured were calibrated to RHE using the following equation: E (V vs. RHE) = E (Hg/HgO) + 0.059 pH + 0.098. Before electrocatalytic experiments were performed, the electrolyte was bubbled by N<sub>2</sub> gas for 30 min to achieve the O<sub>2</sub>-free solution, and the polarization curves were obtained using linear sweep voltammetry with a scan rate of 5 mV s<sup>-1</sup>. For *iR* correction, the uncompensated ohmic resistance value for each electrode in the electrolyte solution was measured. The potential was based on *iR* correction using the equation: E(iR-corrected) = E-*iR*, where *i* is the current and *R* is the uncompensated electrolyte ohmic resistance measured by electrochemical impedance spectroscopy. All experiments were carried out at 25 °C.

**Faradaic efficiency (FE) determination:** The FE was calculated by comparing the amount of measured hydrogen generated by potentiostatic cathode electrolysis (–0.05 V) with calculated hydrogen (assuming 100% FE). 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.

**Computational details:** Spin-polarized density functional theory (SP-DFT) calculations were performed using the Vienna ab initio simulation package (VASP).<sup>1–3</sup> We employed the Perdew-Burke-Ernzerhof (PBE) function for the calculation of the exchange-correlation energy<sup>4</sup> and projector augmented wave (PAW) potentials.<sup>5,6</sup> 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<sup>-1</sup>. The k-point mesh was  $6 \times 6 \times 1$  using Monkhorst-Pack method.<sup>7</sup> The simulations were performed based on a PtO<sub>2</sub>(111) slab model, a Co(OH)F(111) slab model and interface of PtO<sub>2</sub> and Co(OH)F with one PtO<sub>2</sub> unit on the Co(OH)F(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)<sup>8</sup> method was used to examine the energy profiles along selected pathways for H<sub>2</sub>O dissociation.

The free energy change for H adsorption ( $\Delta G_{H^*}$ ) on PtO<sub>2</sub>(111) surface was calculated as follows, which is proposed by Norskov and coworkers:<sup>9</sup>

$$\Delta G_{\rm H} = E_{\rm total} - E_{\rm sur} - E_{\rm H}^2/2 + \Delta E_{\rm ZPE} - T\Delta S \tag{1}$$

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

**Definition of overpotential and Tafel slope:** According to classic electrochemistry books,<sup>10,11</sup> the overpotential ( $\eta$ ) is defined as the difference between the actual applied potential (*E*) and the reversible potential (*E*<sub>r</sub>) of the reaction:

$$\eta = E - E_{\rm r}$$

For the HER,  $E_r$  is 0 V vs. RHE. As a result, HER  $\eta$  equals to the actual applied potential E, which is always a negative quantity. Moreover, according to the Tafel equation ( $\eta = a + b \log|j|$ ), the HER Tafel slope b determined from the Tafel plot ( $\eta$  vs.  $\log|j|$ ) should also be negative. Note that presenting the data in this way is consistent with electrochemistry conventions.

Calculation of Double-layer capacitance ( $C_{dl}$ ), roughness factor ( $\mathbf{R}_{f}$ ), and intrinsic activity:  $C_{dl}$  is estimated by applying the equation:<sup>12</sup>

$$C_{\rm dl} = \Delta j/2 \ v = (j_{\rm a} - j_{\rm c})/2 \ v$$

where  $j_a$  and  $j_c$  are the anodic and cathodic current density, respectively, recorded at a potential of +0.315 V vs. RHE, and v is the scan rate (Fig. S6). The ideal plane electrode has a  $C_{dl}$  of 40  $\mu$ F cm<sup>-2</sup>, and R<sub>f</sub> can be calculated using the equation:<sup>13</sup>

$$R_f = C_{dl}/40$$

the  $j_{\text{specific}}$  is calculated by the equation:<sup>14,15</sup>

where 
$$j_{\text{specific}} = j/R_{\text{f}}$$

where *j* is the HER current density at a potential of -0.1 V vs. RHE.

Analysis of HER mechanism and Tafel slope: Regarding the HER mechanism, two possible

reaction pathways have been proposed.<sup>16,17</sup> (i) The first step is to form electrochemically adsorbed hydrogen ( $H_{ads}$ , Volmer reaction):

H<sup>+</sup> + e<sup>-</sup> 
$$\rightleftharpoons$$
 H<sub>ads</sub> (in acidic solution)  
H<sub>2</sub>O + e<sup>-</sup>  $\rightleftharpoons$  H<sub>ads</sub> + OH<sup>-</sup> (in alkaline solution)  
b = -2.303 · R T/(β·F) ≈ -120 mV dec<sup>-1</sup>

where *R* is the ideal gas constant, *T* is the absolute temperature,  $\beta \approx 0.5$  is the symmetry coefficient, and F is the Faraday constant. A different reaction step in the next pathway leads to a different HER mechanism. To be specific, (ii) the formed H<sub>ads</sub> undergoes an electrochemical desorption step (Heyrovsky reaction):

 $H_{ads} + H^+ + e^- \rightleftharpoons H_2$  (in acidic solution)  $H_{ads} + H_2O + e^- \rightleftharpoons H_2 + OH^-$  (in alkaline solution)  $b = -2.303 \cdot R T/((1+β) \cdot F) \approx -40 \text{ mV dec}^{-1}$ 

or a recombination step (Tafel reaction)

 $H_{ads}$  +  $H_{ads}$  ⇒  $H_2$  (in both acidic and alkaline solutions)  $b = -2.303 \cdot R T/(2 F) \approx -30 \text{ mV dec}^{-1}$ 

For PtO<sub>2</sub>–Co(OH)F, its Tafel slope in 0.1 M KOH was found to be  $-63 \text{ mV dec}^{-1}$ . It can be explained by a formal kinetics approach in two cases: (i) the Heyrovsky mechanism is operative and the adsorption of the reaction intermediate H<sub>ads</sub> proceeds under Temkin conditions in the range of intermediate surface coverages  $0.2 < \theta < 0.8$ ;<sup>18,19</sup> (ii) the mechanism involves a surface chemical rearrangement step H<sub>ads</sub>(A)  $\rightarrow$  H<sub>ads</sub>(B) as the rate determining step (RDS), which features the surface sites A and B having different energy levels.<sup>15,19-21</sup> The latter case supports the proposed hypothesis on the synergy between PtO<sub>2</sub> and Co(OH)F. Accordingly, the following HER mechanism is predicted:

$$H_2O + e^- = H^*(Co-Pt) + OH^-$$
 (1)

$$H^{*}(Co-Pt) \to H^{*}(Pt)$$
 (2)

$$H^{*}(Pt) + H^{*}(Pt) = H_{2}$$
 (3)

If Step 2 representing the surface diffusion of H\* is the RDS, the overall reaction rate is equal to:

$$-j = 2 \mathbf{F} \mathbf{k}_2 \cdot \theta(\mathbf{Co} - \mathbf{Pt}) (1 - \theta(\mathbf{Pt}))$$
(4)

where  $k_{\pm i}$  is the rate constant of step i in the forward (+) or backward (-) direction and  $\theta$  is the fractional occupancy of H-adsorption sites on the PtO<sub>2</sub>–Co(OH)F interface or PtO<sub>2</sub> surface. If we

assume that the Volmer step (Step 1) preceding the RDS is in quasi-equilibrium at low overpotentials, we obtain the following equation:

 $k_1 (1-\theta(Co-Pt)) \exp(-\beta_1 F E/(R T)) = k_1 c(OH^-) \cdot \theta(Co-Pt) \exp((1-\beta_1) F E/(R T)) (5)$ 

where  $\beta$  is the symmetry factor. Since  $\theta$  is close to 0 at low overpotentials, it can be approximated that  $(1-\theta) = 1$ . In that case from Eq. 5 we obtain:

$$\theta(\text{Co-Pt}) = (k_1/k_{-1}) (1/c(\text{OH}^-)) \exp(-F E/(R T))$$
 (6)

Now, by replacing  $\theta$ (Co–Pt) in the rate law of the total reaction (Eq. 4) we get:

$$-j = 2 \operatorname{F} k_2 (k_1/k_{-1}) (1/c(\operatorname{OH}^{-})) \exp(-F E/(R T))$$
(7)

For T = 298 K, the Tafel slope is:

$$b = -2.303 \ R \ T/F = -60 \ mV \ dec^{-1}$$
(8)

At higher overpotentials, i.e. at higher current densities, at which  $\theta \rightarrow 1$ , the reaction pathway involving Step 2 as the chemical RDS reaches a reaction limiting current density,<sup>19</sup> and H\* desorption dominantly proceeds through the Heyrovsky step (electrochemical step):

$$H^{*}(Pt) + H_{2}O + e^{-} = H_{2} + OH^{-}$$
 (9)

Under such conditions, a Tafel slope of about  $-120 \text{ mV dec}^{-1}$  is expected (assuming  $\beta = 0.5$ ) since the overall reaction rate is then given by:

$$-j = 2 F k_9 \exp(-\beta F E/(R T))$$
(10)

The Tafel slope of PtO<sub>2</sub>–Co(OH)F NA/TM (-63 mV dec<sup>-1</sup>) observed at low overpotentials is almost identical to the theoretical one when  $\theta \rightarrow 0$ . Furthermore, we also calculated the Tafel slope of PtO<sub>2</sub>–Co(OH)F NA/TM at higher overpotentials, as presented in Fig. S12. A Tafel slope of –123 mV dec<sup>-1</sup> is observed on PtO<sub>2</sub>–Co(OH)F NA/TM at high overpotentials, which is also consistent with the theoretically calculated slope. The Tafel slope of –149 mV dec<sup>-1</sup> detected for Co(OH)F NA/TM at low current densities (Fig. 3b) indicates Step 1 (Volmer reaction) as the RDS. Obviously, the decoration of Co(OH)F NA with PtO<sub>2</sub> nanoparticles modifies the H adsorption properties of the catalyst surface and alters the operative HER mechanism. All these results further demonstrate the proposed alkaline HER mechanism on PtO<sub>2</sub>–Co(OH)F NA/TM.



Fig. S1. The SEM image of TM.



Fig. S2. The HRTEM image of Co(OH)F.



Fig. S3. The HRTEM image of Co(OH)F.



Fig. S4. EDX elemental mapping images of PtO<sub>2</sub>–Co(OH)F NA/TM.



Fig. S5. LSV curves of as-prepared samples at 1.0 M KOH (a) and 30 wt% KOH (b).



**Fig. S6.** CV curves and corresponding capacitive current densities at +0.315 V vs. RHE against scan rate for PtO<sub>2</sub>–Co(OH)F NA/TM (a,b), Co(OH)F NA/TM (c,d) and PtO<sub>2</sub>/TM (e,f).



**Fig. S7.** The multi-current curve of  $PtO_2$ -Co(OH)F NA/TM measured at the current densities between -10 and -100 mA cm<sup>-2</sup> with an increment of -10 mA cm<sup>-2</sup> per 500 s.



Fig. S8. SEM images of PtO<sub>2</sub>–Co(OH)F NA/TM after long-term stability test for 50 h.



Fig. S9. HRTEM image of PtO<sub>2</sub>–Co(OH)F after durability test.



Fig. S10. XPS spectrum in Pt 4f region for PtO<sub>2</sub>–Co(OH)F after long-term durability test.



Fig. S11. The amount of gas theoretically calculated and experimentally measured from  $PtO_2$ -Co(OH)F NA/TM vs. time for HER.



**Fig. S12** Tafel plots of PtO<sub>2</sub>–Co(OH)F NA/TM at low (red line) and high (green line) overpotentials.

Catalyst	$\eta$ at -4 mA cm <sup>-2</sup>		$\eta$ at –100 mA cm <sup>-2</sup>			
	( <b>mV</b> )		(mV)		Loading <sup>a</sup>	Ref
	0.1 M	1.0 M	0.1 M	1.0 M	(µg cm <sup>-2</sup> )	iver,
	КОН	КОН	КОН	КОН		
PtO2-Co(OH)F NA/TM	-39	-44	-160	-194	54(Pt)	This work
Pt NWs/SL–Ni(OH) <sub>2</sub>	~57	~80		_	15.8(Pt)	[22]
Pt(110)/Ni(OH)2	-110		_	_	Pt electrode	[23]
Pt <sub>3</sub> Ni/C	~57		_	_	1.5(Pt)	[24]
Pt-Ni/C	-40			_	25.5(Pt)	[25]
Pt <sub>13</sub> Cu <sub>73</sub> Ni <sub>14</sub> /CNF@CF	_	-100		_	25(Pt)	[26]
hcp-Pt-Ni	-43			_	7.7(Pt)	[27]
Pt(111)-Co(OH) <sub>2</sub>	~-210			_	Pt electrode	[28]
Pt <sub>3</sub> Ni <sub>2</sub> NWs-S/C	~60	~-37			15.3(Pt)	[29]
Pt@2D-Ni(OH)2	~-100				1.13(Pt)	[30]
Ni <sub>3</sub> N/Pt	_	_		~-110	~300(Pt)	[31]
Pd-Pt-S	_	~40			~20(Pt)	[32]
Mesoporous Pt-Fe	_			~-225	~120(Pt)	[33]
NiP <sub>2</sub> NS/CC	_		_	~-220	4300(cat.)	[34]
CoMn-S@NiO/CC	—	_	_	~-300	6900(cat.)	[35]
Ni <sub>2</sub> P NF/CC	—	_	_	~-400	920(cat.)	[36]
Ni3N NA/CC	_			~-310	1900(cat.)	[37]

**Table S1.** Comparison of HER performance for  $PtO_2$ -Co(OH)F NA/TM with other recently reported Pt-based catalysts.

<sup>a</sup> The 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. Furthm üller, *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. Jónsson, 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 E. Gileadi, *Electrode Kinectics for Chemists, Chemical Engineers and Materials Scientists*, Wiley-VCH, New York, 1993.
- A. J. Bard and L. R. Faulkner, *Electrochemical Methods: Fundamentals and Applications*, Wiley, New York, 2rd Edition, 2000.
- 12 C. C. L. McCrory, S. Jung, J. C. Peters and T. F. Jaramillo, J. Am. Chem. Soc., 2013, 135, 16977–16987.
- 13 S. Levine and A. L. Smith, *Discuss. Faraday Soc.*, 1971, **52**, 290–301.
- B. M. Jović, V. D. Jović, U. Č. Lačnjevac, L. Gajić-Krstajić and N. V. Krstajić, *Int. J. Hydrogen Energy*, 2015, 40, 10480–10490.
- B. M. Jović, V. D. Jović, U. Č. Lačnjevac, S. I. Stevanović, J. Kovač, M. Radović and N. V. Krstajić, *J. Electroanal. Chem.*, 2016, **766**, 78–86.
- 16 B. E. Conway and B. V. Tilak, *Electrochim. Acta*, 2002, **47**, 3571–3594.
- 17 Y. Zheng, Y. Jiao, M. Jaroniec and S. Z. Qiao, Angew. Chem., Int. Ed., 2015, 54, 52–65.
- 18 U. Č. Lačnjevac, B. M. Jović, V. D. Jović, V. R. Radmilović and N. V. Krstajić, Int. J. Hydrogen Energy, 2013, 38, 10178–10190.
- 19 A. Kahyarian, B. Brown and S. Nesic, J. Electrochem. Soc., 2017, 164, H365–H374.
- I. M. Kodintsev and S. Trasatti, *Electrochim. Acta*, 1994, **39**, 1803–1808.
- U. Č. Lačnjevac, V. V. Radmilović, V. R. Radmilović and N. V. Krstajić, *Electrochim. Acta*, 2015, 168, 178–190.

- H. Yin, S. Zhao, K. Zhao, A. Muqsit, H. Tang, L. Chang, H. Zhao, Y. Gao and Z. Tang, *Nat. Commun.*, 2015, 6, 6430.
- R. Subbaraman, D. Tripkovic, D. Strmcnik, K. C. Chang, M. Uchimura, A. P. Paulikas, V. R.
   Stamenkovic and N. M. Markovic, *Science*, 2011, **334**, 1256–1260.
- 24 C. Chen, Y. Kang, Z. Huo, Z. Zhu, W. Huang, H. L. Xin, J. D. Snyder, D. Li, J. A. Herron, M. Mavrikakis, M. Chi, K. L. More, Y. Li, N. M. Markovic, G. A. Somorjai, P. Yang and V. R. Stamenkovic, *Science*, 2014, **343**, 1339–1343.
- R. Kavian, S.-I. Choi, J. Park, T. Liu, H.-C. Peng, N. Lu, J. Wang, M. J. Kim, Y. Xia and S. W.
   Lee, *J. Mater. Chem. A*, 2016, 4, 12392–12397.
- 26 Y. Shen, A. C. Lua, J. Xi and X. Qiu, ACS Appl. Mater. Interfaces, 2016, 8, 3464–3472.
- Z. Cao, Q. Chen, J. Zhang, H. Li, Y. Jiang, S. Shen, G. Fu, B. Lu, Z. Xie and L. Zheng, *Nat. Commun.*, 2017, 8, 15131.
- R. Subbaraman, D. Tripkovic, K. C. Chang, D. Strmcnik, A. P. Paulikas, P. Hirunsit, M. Chan,
  J. Greeley, V. R. Stamenkovic and N. M. Markovic, *Nat. Mater.*, 2012, 11, 550–557.
- P. Wang, X. Zhang, J. Zhang, S. Wan, S. Guo, G. Lu, J. Yao and X. Huang, *Nat. Commun.*, 2017, 8, 14580.
- 30 L. Wang, Y. Zhu, Z. Zeng, C. Lin, M. Giroux, L. Jiang, Y. Han, J. Greeley, C. Wang and J. Jin, *Nano Energy*, 2017, **31**, 456–461.
- 31 Y. Wang, L. Chen, X. Yu, Y. Wang and G. Zheng, *Adv. Energy Mater.*, 2017, 7, 1601390.
- 32 J. Fan, K. Qi, L. Zhang, H. Zhang, S. Yu and X. Cui, ACS Appl. Mater. Interfaces, 2017, 9, 18008–18014.
- E. Isarain-Chavez, M. D. Baro, C. Alcantara, S. Pane, J. Sort and E. Pellicer, *ChemSusChem*, 2017, DOI: 10.1002/cssc.201701938.
- 34 P. Jiang, Q. Liu and X. Sun, *Nanoscale*, 2014, **6**, 13440–13445.
- 35 Q. Li, Z. Xing, D. Wang, X. Sun and X. Yang, ACS Catal., 2016, 6, 2797–2801.
- 36 D. Liu, T. Liu, L. Zhang, F. Qu, G. Du, A. M. Asiri and X. Sun, J. Mater. Chem. A, 2017, 5, 3208–3213.
- Q. Liu, L. S. Xie, F. L. Qu, Z. Liu, G. Du, A. M. Asiri and X. P. Sun, *Inorg. Chem. Front.*, 2017, 4, 1120–1124.