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Electronic Supplementary Information

In situ conversion of layered double hydroxide array into nanoflower of Ni_xV_{1-x}-MOF as a highly efficient and stable electrocatalyst for oxygen evolution reaction

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Materials

Ethanol (C_2H_5OH) was bought from Chengdu Changlian Chemical Reagent Co., Ltd. (Chengdu, China). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) were provided by Chengdu Kelong Chemical Reagent Factory (Chengdu, China). Hydrochloric acid (HCl), nickel nitrate hexahydrate ($Ni(NO_3)_2{\cdot}6H_2O$), ammonium metavanadate (NH_4VO_3), ammonium fluoride (NH_4F), urea ($CO(NH_2)_2$), N, N-Dimethylformamide (DMF) and p-benzenedicarboxylic acid ($C_8H_4O_4$) were purchased from Aladdin Ltd. (Shanghai, China). $RuCl_3{\cdot}3H_2O$, and a Nafion (5 wt%) solution were obtained from Sigma-Aldrich Chemical Reagent Co., Ltd. (Shanghai, China). Nickel foam (NF) was purchased from Shenzhen Green and Creative Environmental Science and Technology Co., Ltd. (Shenzhen, China), and was pretreated in HCl, deionized water and ethanol several times to ensure the surface impurities removed. All above reagents and chemicals were used as received without further purification and the water used throughout all experiments was purified through a Millipore system.

Preparation of precursor

NiV-LDH was prepared according to previous work with minor modifications. Firstly, 2 mmol $Ni(NO_3)_2{\cdot}6H_2O$, 0.25 mmol NH_4VO_3, 10 mmol $CO(NH_2)_2$, and 4 mmol NH4F were added in 40 mL ultrapure water. After vigorous magnetically stirred for 10 min, as-formed pellucid solution was transferred to a 50 mL Teflon-lined stainless-steel autoclave with a piece of cleaned NF (2 cm × 4 cm). Secondly, the autoclave was sealed and maintained at 120 °C for 6 h in an electric oven and then cooled down naturally to room temperature. Thirdly, the NF covered with yellow green products was taken out and then washed with ultrapure water and ethanol several times before dring at 70 °C for 3 h in an electric oven.

Preparation of $Ni_{0.9}V_{0.1}$-MOF

1.75 mmol $C_8H_4O_4$, 2.5 mmol $Ni(NO_3)_2·6H_2O$, and 0.25 mmol NH_4VO_3 were dissolved in 35 mL DMF under vigorous stirring to form a uniform solution. Then, 2.5 mL C_2H_5OH and 2.5 mL H_2O were added in dropwise to the solution under constant stirring for 30 min. Then, the pellucid solution was transferred to a 50 mL Teflon–lined stainless–steel autoclave with a piece of NiV-LDH (2 cm × 4 cm). The autoclave was sealed and maintained at 120 °C for 12 h in an electric oven. After cooled down naturally to room temperature, the sample was taken out and washed with distilled water and ethanol several times, followed by drying at 70 °C for 3 h in vacuum. Ni_xV_{1-x}-MOF on NF with varied Ni/V atomic ratios of 1.00/0.00, 0.95/0.05, and 0.80/0.20 were also prepared by adjusting the Ni/V salt amount, ensuring the total mole number of Ni element added with V element is 2.75 mmol without any other variations, and the corresponding samples are denoted as Ni-MOF, $Ni_{0.95}V_{0.05}$-MOF, and $Ni_{0.8}V_{0.2}$-MOF, respectively.

Synthesis of RuO_2

RuO_2 was prepared according to previous publication. Briefly, 2.61 g of $RuCl_3·3H_2O$ and 30.0 mL KOH (1.0 M) were added into 100 mL distilled water and stirred for 45 min at 100 °C. Then the above solution was centrifuged for 10 minutes and filtered.

The precipitates were collected and washed with water several times. Finally, the product was dried at 80 °C overnight and then annealed at 300 °C in air atmosphere for 3 h. For a typical synthesis of RuO_2/NF electrode, 50 mg RuO_2 was dispersed in 1 mL ethane/water (v:v = 1:1) solution with sonication for 30 min. Then 8.9 μL catalytic inks were dropped on NF (0.5 × 0.5 cm), and dried at 80 °C for 4 h.

Characterizations

Powder X-ray diffraction (XRD) patterns were performed using a RigakuD/MAX 2550 diffractometer with Cu Kα radiation (λ=1.5418 Å). Fourier transform infrared (FT-IR) transmission spectrum was collected on a Nicolet–6700 spectrometer using the potassium bromide pellet method. Raman spectrum was recorded on a LABRAM HR micro–Raman spectroscope with an excitation wavelength of 532 nm. Scanning electron microscope (SEM) measurements were recorded on a XL30 ESEM FEG scanning electron microscope at an accelerating voltage of 20 kV. The structures of the samples were determined by Transmission electron microscopy (TEM) images on a HITACHI H-8100 electron microscopy (Hitachi, Tokyo, Japan) operated at 200 kV. Xray photoelectron spectroscopy (XPS) data of the samples was collected on an ESCALABMK II x- ray photoelectron spectrometer using Mg as the exciting source.

Electrochemical measurement

Electrochemical measurements were performed with a CHI 660E electrochemical analyzer (CH Instruments, Inc., Shanghai) in a standard three-electrode system. $Ni_{0.9}V_{0.1}$-MOF was used as the working electrode. Graphite plate, and an Hg/HgO were used as the counter electrode and the reference electrode, respectively. The temperature of solution was kept at 25 °C for all the measurements via the adjustment of air condition and heating support, which ensured the variation of diffusion coefficient below 1%. The potentials reported in this work were calibrated to RHE other than especially explained, using the following equation: E (RHE) = E (Hg/HgO) + (0.098 + 0.059 pH) V. In this communication, all the data are measured several times.

The calculation of TOF: TOF= (J×A)/(m×F×n), where, J (mA cm-2) is the measured current density at given overpotential; A is the surface area of GC electrode (0.07065 cm2); m is the number of electrons (OER m=4 and HER m=2); F is faraday constant (96485.3 C mol^{-1}) and n is the total mole of the metal atoms on the electrode (assuming that every metal atom is involved in the catalysis).

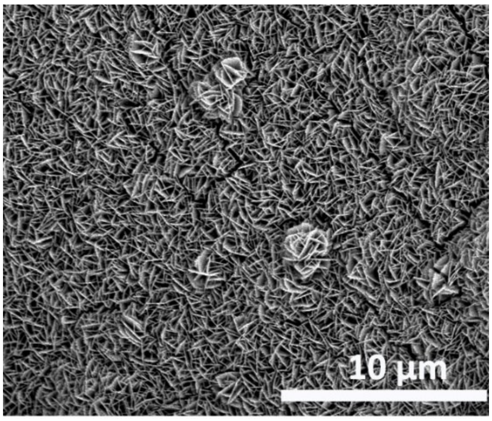
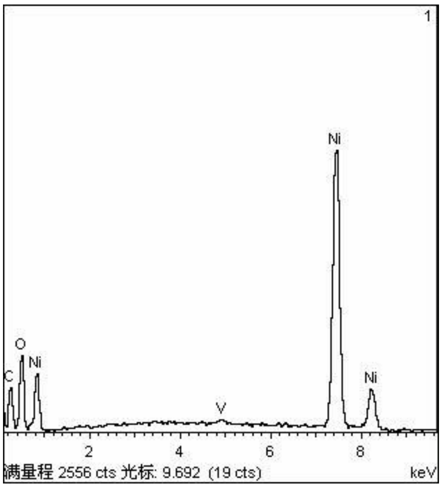


Fig. S1. SEM images of NiV-LDH.



Element	Wt%	At%
C K	1.10	45.61
O K	0.60	24.02
V K	0.13	0.17
Ni K	1.03	30.20

Fig. S2. Content of each element.

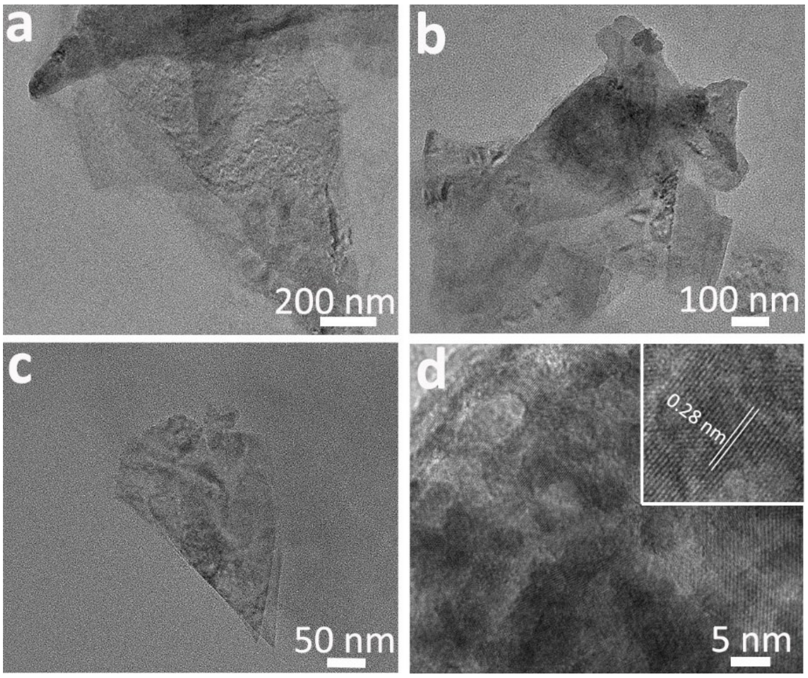


Fig. S3. The TEM images of $Ni_{0.9}V_{0.1}$-MOF in different scale and the correspondent HRTEM image.

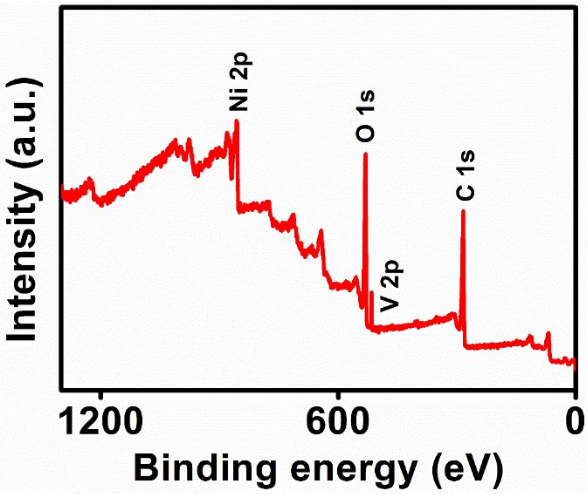


Fig. S4. XPS survey spectrum for $Ni_{0.9}V_{0.1}$-MOF.

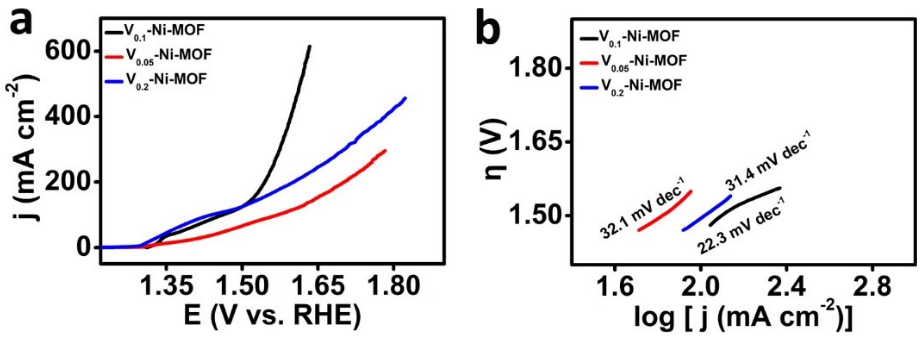


Fig. S5. (a) LSV curves of Ni$_{0.9}$V$_{0.1}$-MOF, Ni$_{0.8}$V$_{0.2}$-MOF and Ni$_{0.95}$V$_{0.05}$-MOF with a scan rate of 5 mV s^{-1} for water oxidation. (b) Tafel plots for Ni$_{0.9}$V$_{0.1}$-MOF, Ni$_{0.8}$V$_{0.2}$-MOF and Ni$_{0.95}$V$_{0.05}$-MOF.

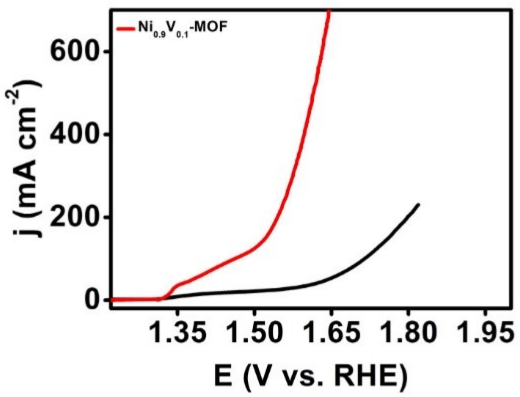


Fig. S6. LSV curves of no precursor material and $Ni_{0.9}V_{0.1}$-MOF with a scan rate of 5 mV s^{-1} for water oxidation.

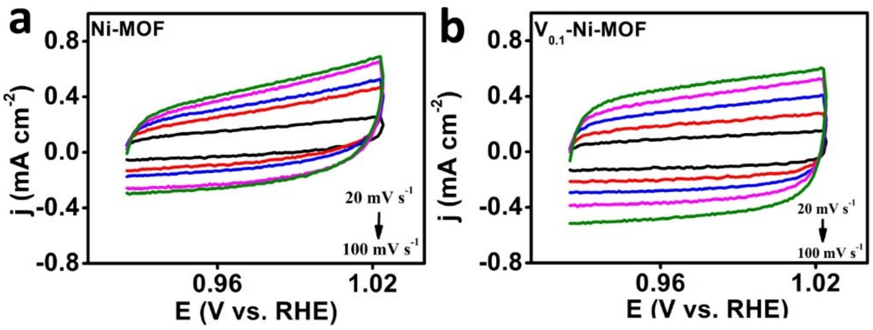


Fig. S7. CVs of (a) Ni-MOF (b) $Ni_{0.9}V_{0.1}$-MOF with various scan rates.

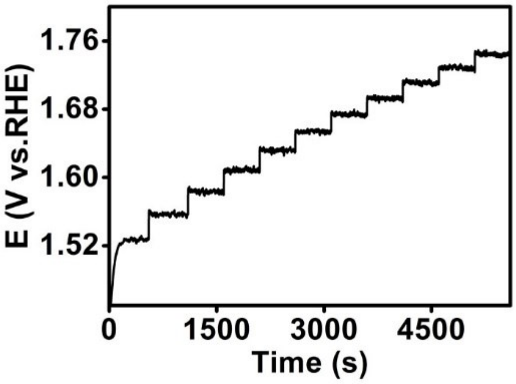


Fig. S8. Multi-step chronopotentiometric curve for $Ni_{0.9}V_{0.1}$-MOF.

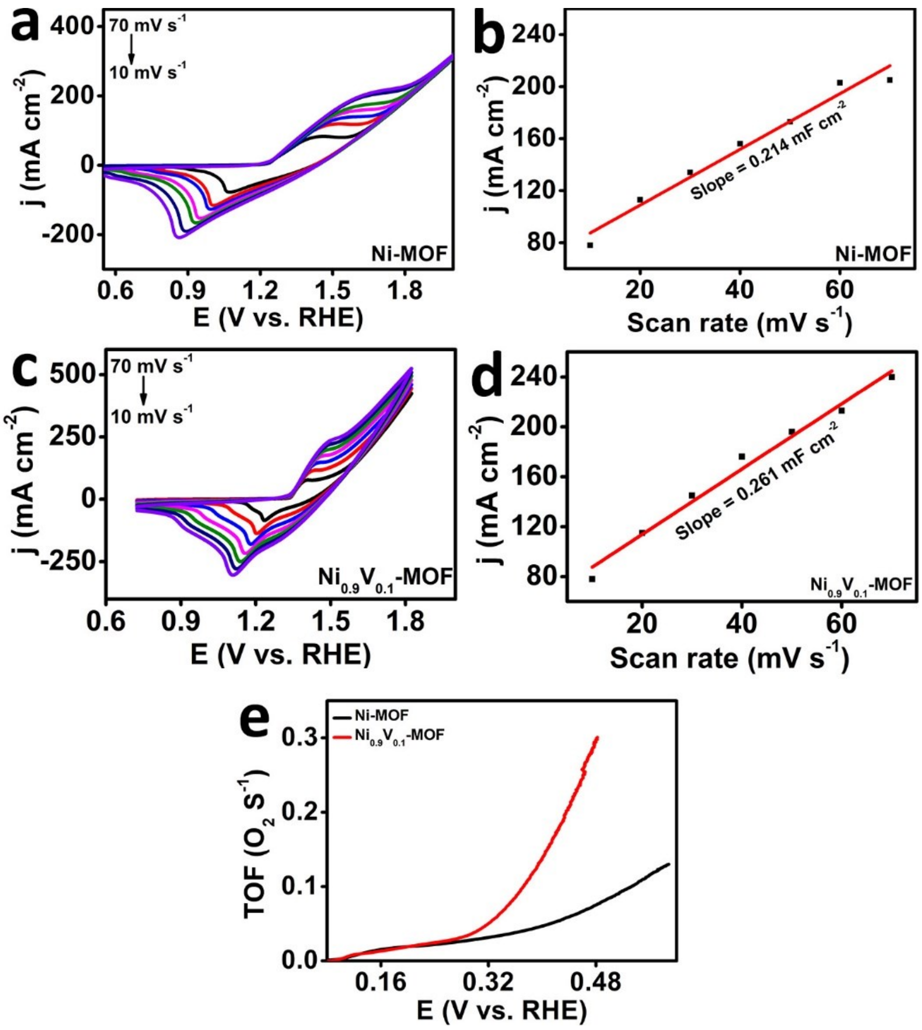


Fig.S9. (a) CVs for Ni-MOF in the faradaic capacitance current range at scan rates from 10 to 70 mV s^{-1} in 1.0 M KOH at room temperature. (b) Oxidation peak current versus scan rate plot for Ni-MOF. (c) CVs for $Ni_{0.9}V_{0.1}$-MOF in the faradaic capacitance current range at scan rates from 10 to 70 mV s^{-1} in 1.0 M KOH at room temperature. (d) Oxidation peak current versus scan rate plot for $Ni_{0.9}V_{0.1}$-MOF. The slope is given by the formula[1]: slope = $n^2F^2m/4RT$, where n representing the amount of electron transfer is 1 assuming a one-electron process for the oxidation of metal centers in Co-MOF, F is the Faradaic constant, m is the number of active species, and R and T are the ideal gas constant and the absolute temperature, respectively. (e) Plot of the TOF of $Ni_{0.9}V_{0.1}$-MOF and Ni-MOF as a function of the overpotential. The TOF is calculated according to the literature[1] by the following formula: TOF = JA/4Fm (J is the current density; A is the geometrical electrode area, and 4 expresses the moles of electron consumption for one mole oxygen evolution). We figured out the TOF for Ni-MOF and $Ni_{0.9}V_{0.1}$-MOF as 0.05 mol O_2 s^{-1} and 0.138 mol O_2 s^{-1} at an overpotential of 400 mV, respectively.

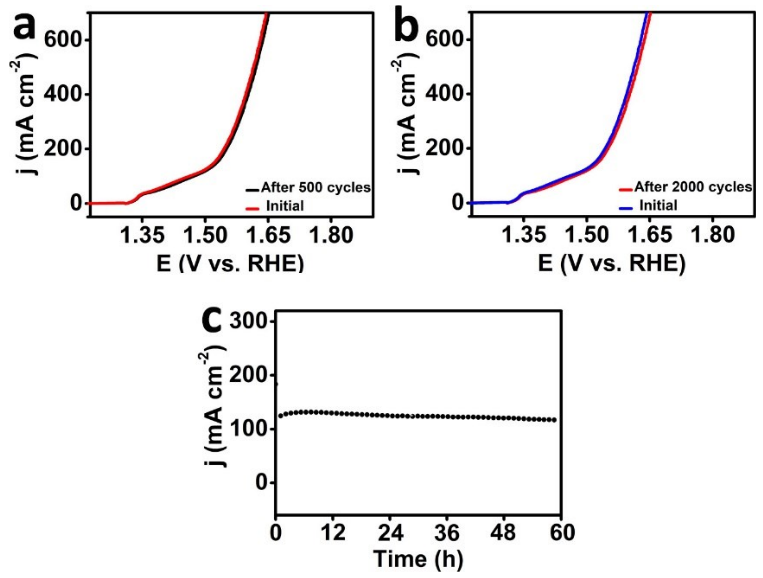


Fig S10. (a) LSV curves for $Ni_{0.9}V_{0.1}$-MOF before and after 500 CV cycles. (b) LSV curves for $Ni_{0.9}V_{0.1}$-MOF before and after 2000 CV cycles. (c) Time-dependent current density curve of $Ni_{0.9}V_{0.1}$-MOF under static overpotential of 120 mV for at least 60 h.

Table S1. Comparison of OER performance for $Ni_{0.9}V_{0.1}$-MOF with other typical non-noble-metal electro-catalysts documented in literature (electrolyte: 1.0 M KOH).

Catalyst	j (mA cm^{-2})	η (mV)	Electrolyte	Ref.
$V_{0.1}$-Ni-MOF	100/150	232/290	1.0 M KOH	This work
Ni-MOF	100/150	310/380	1.0 M KOH	
Co-MOF/NF	100	311	1.0 M KOH	1
NiFe-MOF-74 rhombic crystals/NF	100	390	1.0 M KOH	2
NiPc-MOF modified FTO	100	390	1.0 M KOH	3
ultrathin NiFe-MOF film	150	330	1.0 M KOH	4
MOF derived Co_3O_4 NA/CF	15	308	1.0 M KOH	5
$Ni_{0.75}V_{0.25}$-LDH	57	350	1.0 M KOH	6
$NiCo_2S_4$ NA/CC	100	340	1.0 M KOH	7
Co_3O_4-MTA	150	360	1.0 M KOH	8
$MnCo_2S_4$ NA/TM	50	325	1.0 M KOH	9
$CuCo_2S_4$/CF	100	295	1.0 M KOH	10
Cu_3P@NF	10	320	1.0 M KOH	11
$NiPS_3$	10	294	1.0 M KOH	12
Ni@graphene	10	370	1.0 M KOH	13
Ni_2P	10	290	1.0 M KOH	14
NiS@N/S-C	10	471	1.0 M KOH	15

References

1 X. Zhang, W. Sun, H. Du, R. Kong and F. Qu, *Inorg. Chem. Front.*, 2018, **5**, 344–347.

2 J. Xing, K. Guo, Z. Zou, M. Cai, J. Du and C. Xu, *Chem. Commun.*, 2018, **54**, 7046–7049.

3 H. Jia, Y. Yao, J. Zhao, Y. Gao, Z. Luo and P. Du, *J. Mater. Chem. A*, 2018, **6**, 1188–1195.

4 J. Duan, S. Chen and C. Zhao, *Nat. Commun.*, 2017, **8**, 15341–15348.

5 Y. Wei, X. Ren, H. Ma, X. Sun, Y. Zhang, X. Kuang, T. Yan, H. Ju, D. Wu and Q. Wei, *Chem. Commun.*, 2018, **54**, 1533–1536.

6 K. Fan, H. Chen, Y. Ji, H. Huang, P. M. Claesson, Q. Daniel, B. Philippe, H.Rensmo, F. Li, Y. Luo and L. Sun, *Nat. Commun.*, 2016, **7**, 11981.

7 D. Liu, Q. Lu, Y. Luo, X. Sun and A. M. Asiri, *Nanoscale*, 2015, **7**, 15122–15126.

8 T. Ma, J. Cao, M. Jaroniec and S. Qiao, *Angew. Chem. Int. Ed.*, 2016, **55**, 1138–1142.

9 X. Zhang, C. Si, X. Guo, R. Kong and F. Qu, *J. Mater. Chem. A*, 2017, **5**, 17211–17215.

10 L. Yang, L. Xie, X. Ren, Z. Wang, Z. Liu, G. Du, A. M. Asiri, Y. Yao and X. Sun, *Chem. Commun.*, 2018, **54**, 78–81.

11 A. Han, H. Zhang, R. Yuan, H. Ji and P. Du, *ACS Appl. Mater. Interfaces*, 2017, **9**, 2240–2248.

12 S. Xue, L. Chen, Z. Liu, H. Cheng and W. Ren, *ACS Nano*, 2018, **12**, 5297–5305.

13 L. Ai, T. Tian and J. Jiang, *ACS Sustain. Chem. Eng.*, 2017, **5**, 4771–4777.

14 L.Stern, L. Feng, F. Song and X. Hu, *Energy Environ. Sci.*, 2015, **8**, 2347–2351.

15 L. Yang, M. Gao, B. Dai, X. Guo, Z. Liu and B. Peng, *Electrochim. Acta*, 2016, **191**, 813–820.