Electronic Supplementary Information

One-step CVD synthesis of carbon framework wrapped Co_2P as flexible electrocatalyst for efficient hydrogen evolution

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1. Experimental section

1.1. Chemicals and reagents

Nafion (5 wt %), dimethylformamide (DMF), and Pt/C (20 wt % Pt on Vulcan XC-72R) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd. Carbon cloth (CC) was obtained from Wuhan Instrument Surgical Instruments Business. Cobalt chloride hexahydrate ($CoCl_2·6H_2O$), potassium phosphate (K_3PO_4), and polyvinylpyrrolidone (PVP) were purchased from Sinopharm Chemical Reagent Co., Ltd. Sodium dodecyl benzene sulfonate (SDBS), isooctane (C_8H_{18}), and n-butyl alcohol ($C_4H_{10}O$) were purchased from Aladdin Industrial Co., Ltd. All chemicals are analytical reagent grade and were used as received. Ultrapure water (18.2 MΩ cm) was used throughout the whole work.

2.2. Instrumentation

The structures and morphologies of prepared nanohybrids were sequentially assessed using field-emission scanning electron microscopy (FESEM, JEOL-7800F, Japan Electron Optics Laboratory Co., Japan), energy-dispersive X-ray spectroscopy (EDX, INCA X-Max 250, Japan), and transmission electron microscope (TEM, JEM-2100, Japan). Powder X-ray diffraction (XRD, Shimadzu XRD-7000, Shimadzu, Japan) patterns were executed by the XRD-7000 with Cu Kα source radiation at a scanning rate of 2° min^{-1} from 10° to 80°. Raman spectrum (Renishaw, UK) was recorded over the frequency range of 1000-3000 cm^{-1} using a 532.8 nm laser with an Invia Refl under ambient conditions. The surface properties of resultant nanohybrids were analyzed with X-ray photoelectron spectroscopy (XPS, Thermo ESCALAB 250Xi, Thermoelectricity Instruments, USA), and the thermal decomposition was investigated through thermogravimetric analyser (TGA, TA Instruments, USA) at a heating rate of 5 °C min^{-1} from 25 to 700 °C in air flow.

2.3. Construction of the $Co_3(PO_4)_2$ precursor

$CoCl_2$ (6 mL, 0.45 mol L^{-1}) aqueous solution was added to the mixture of SDBS (1.5 g), C_8H_{18} (36 mL), and $C_4H_{10}O$ (12 mL) under ultrasound for 15 min at room temperature to construct the micro-emulsion system. Next, the K_3PO_4 (6 mL, 0.3 mol L^{-1}) aqueous solution was further added in the above micro-emulsion system slowly for 2 min followed by ultrasound for 30 min at room temperature. After the deposition reaction finished, the mixture was washed several times *via* centrifugation at 8000 rpm for 5 min with ethanol and ultrapure water, and then dried under vacuum at 60 °C. The mixture was further annealed at 650 °C with a rising rate of 5 °C min^{-1} and maintained for 3 h to remove the crystal water, eventually forming $Co_3(PO_4)_2$ as a precursor for further work.

2.4. Construction of Co_2P@C/CC *via* one-step CVD method

A piece of CC (2 cm × 1 cm) was preprocessed with concentrated HNO_3 and then sequentially rinsed by ethanol and ultrapure water for each 10 min, thus acquiring the clean CC. The weight of CC was recorded after drying at 60 °C for 5 h. The preprocessed CC was dipped in an ink with the mixture of 0.5 g of $Co_3(PO_4)_2$, 0.2 g of PVP, and 5 mL of DMF for 5 min, then withdrawn from the ink, followed by dried at 80 °C for 0.5 h. The obtained sample was put in a ceramic boat and heated to 750 °C in a tube furnace under Ar atmosphere. Then hydrogen gas (Ar: hydrogen=5:1) was introduced into the furnace for 10 min to reduce the $Co_3(PO_4)_2$ to Co_2P. Immediately, 350 sccm C_2H_4 was replenished for 30 min to conduct the favourable synthesis of Co_2P@C/CC. The resultant product was rapidly cooled down to room temperature under the flow of Ar atmosphere. For the preparation of Co_2P/CC without wrapped carbon framework, the same procedure was executed except pumping C_2H_4.

2.5. Electrochemical performance

The electrochemical tests were executed by a workstation (CHI660E, CHI Instruments Inc, Shanghai) in a three-electrode system coupled with Co_2P@C/CC as a working electrode, platinum foil as a counter electrode and saturated calomel electrode (SCE) as a reference electrode. The polarization curves were surveyed *via* the linear sweep voltammetry (LSV) at a scan rate of 2 mV s^{-1}, and the long-term durability was investigated using potentiostatic electrolysis at fixed potentials. The onset overpotentials were ascertained up to the initiate of linear region in Tafel plot. Pt/C ink was prepared by dissolving 5 mg of

Pt/C into 300 μL of ethanol containing 1 wt % Nafion. Then 66 μL of above ink was deposited on the surface of 1 cm^2 CC and the Pt/C/CC was air-dried at room temperature. The current density was calibrated corresponding to the geometric area of working electrode. The geometric area values of all the samples are all 1 cm^2. The value of current density is calculated *via* dividing the current by geometric area. The recorded potential was adjusted by this equation: E (RHE) = E (SCE) + (0.242+ 0.059 pH) V.

2. Results

Calculation for the percent content of Co_2P in the Co_2P@C/CC.

As depicted in Figure 2B, the TGA curve of the resultant product shows a weight loss of 96.06 % in the temperature range from 600 °C to 800 °C, which is ascribed to the decomposition of Co_2P@C/CC to yield Co_3O_4. So, the percent content of Co_2P in the Co_2P@C/CC can be calculated as follows:

$$\text{Content } (Co_2P)\ \% = \frac{(1 - 96.06\%) \times {}^{3Mr(Co)}/_{Mr(Co_3O_4)}}{{}^{2Mr(Co)}/_{Mr(Co_2P)}} \times 100 = 3.65,$$

where *Mr* denotes the relative molecular mass.

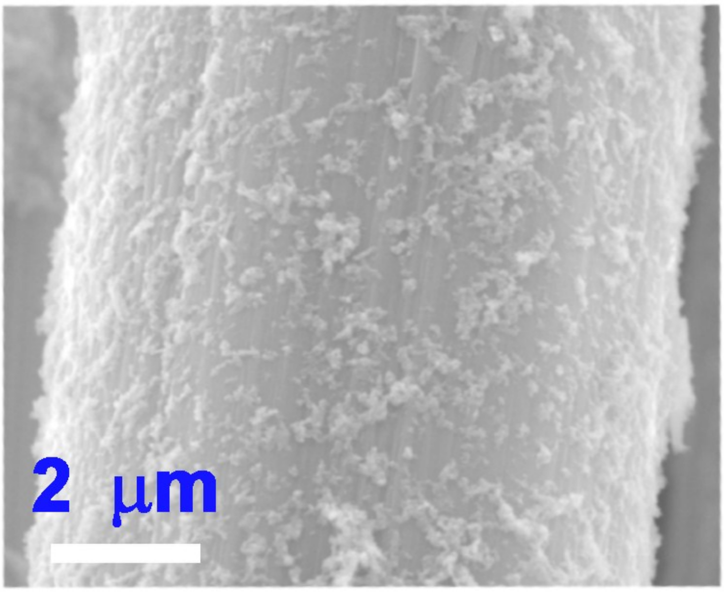

Fig. S1 SEM image of $Co_3(PO_4)_2$/CC.

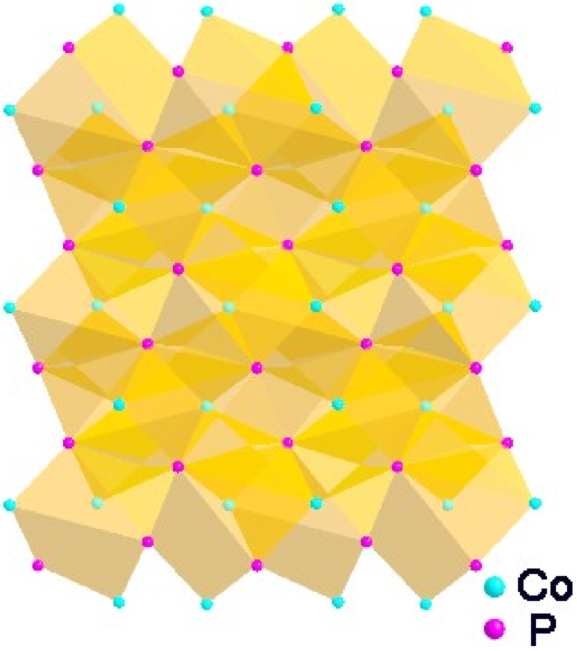

Fig. S2 Crystal structure of CoP.

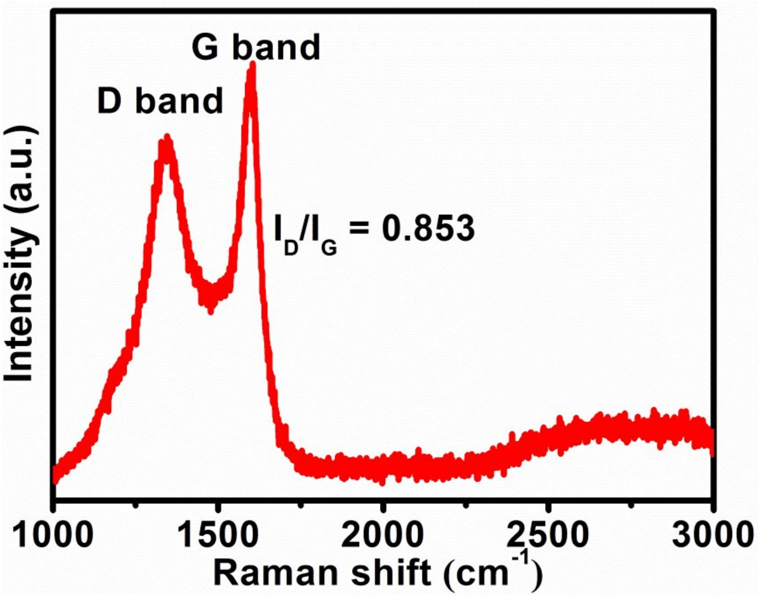

Fig. S3 The Raman spectrum of Co_2P@C.

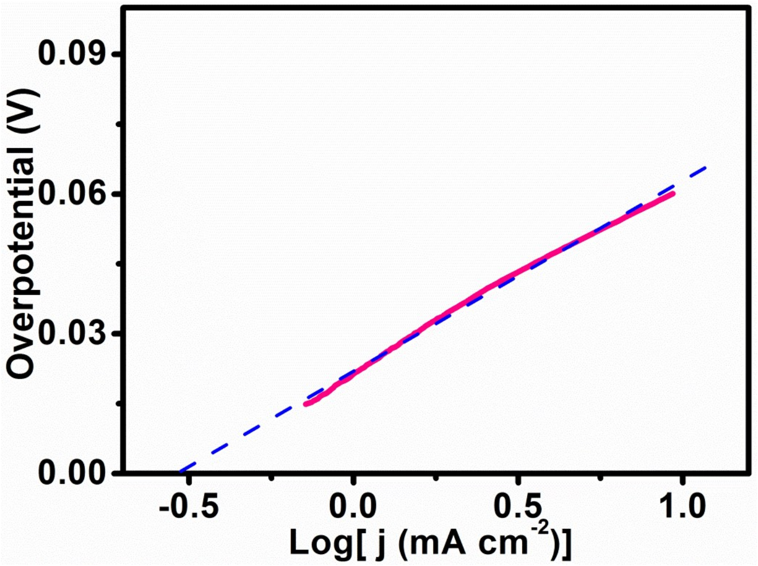

Fig. S4 The exchange current density of Co_2P@C/CC *via* applying extrapolation method to the Tafel plot.

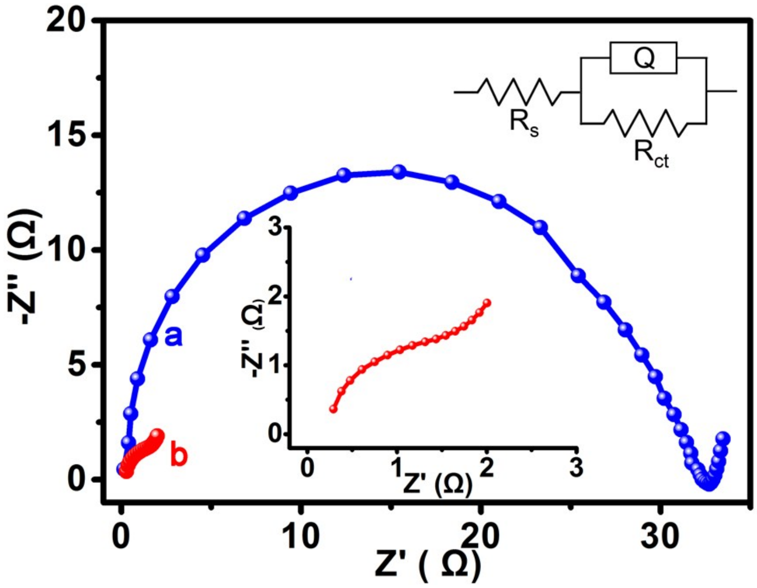

Fig. S5 Nyquist plots of a) Co_2P/CC and b) Co_2P@C/CC in 0.5 M H_2SO_4 with a fitted equivalent circuit (inset).

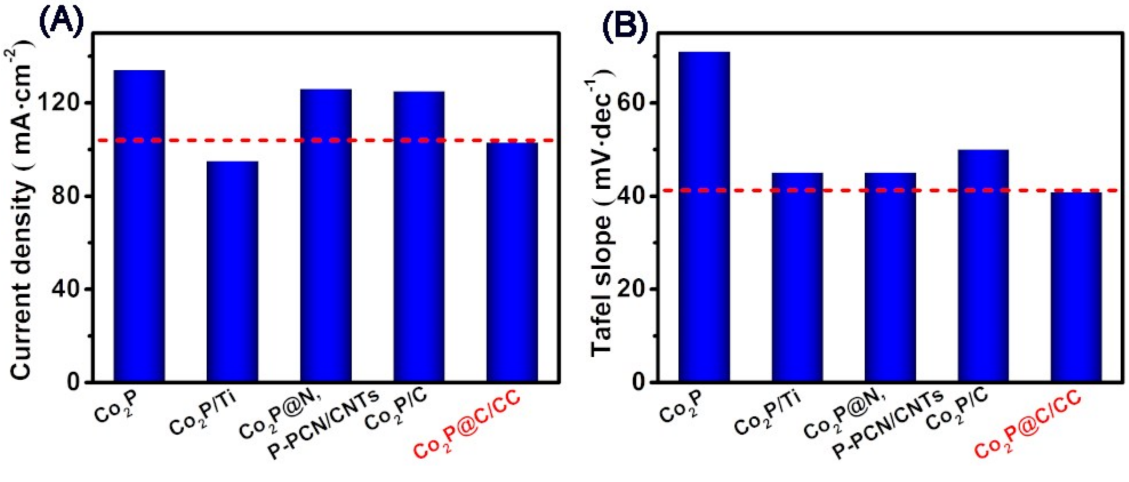

Fig. S6 Comparison of HER performance of Co_2P@C/CC with that of representative dicobalt phosphide in acid electrolyte.

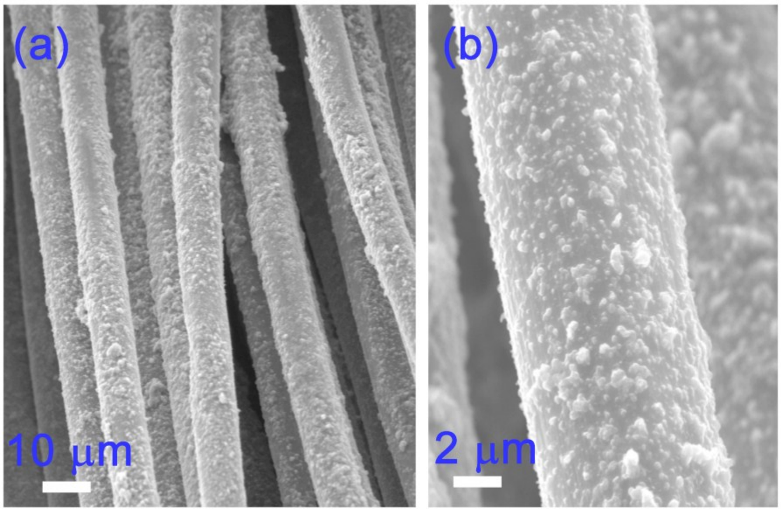

Fig. S7 SEM images of Co_2P@C/CC at low (a) and high (b) magnification after electrochemical tests.

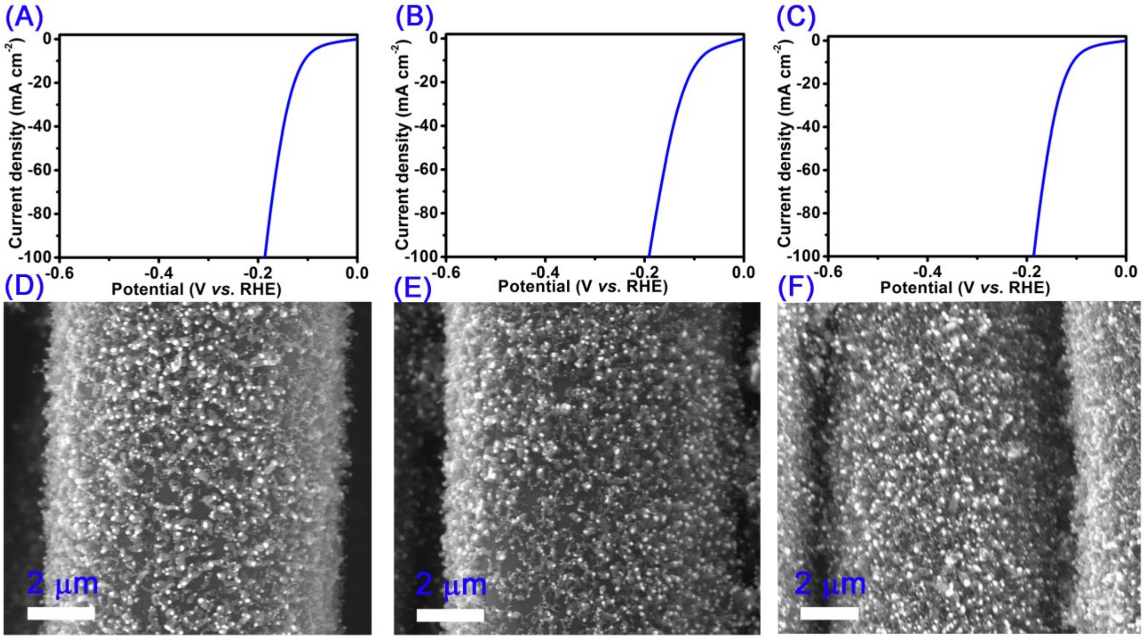

Fig. S8 (A-C) Polarization curves for Co_2P@C/CC of three different samples, (D-F) the corresponding SEM images of the three samples.

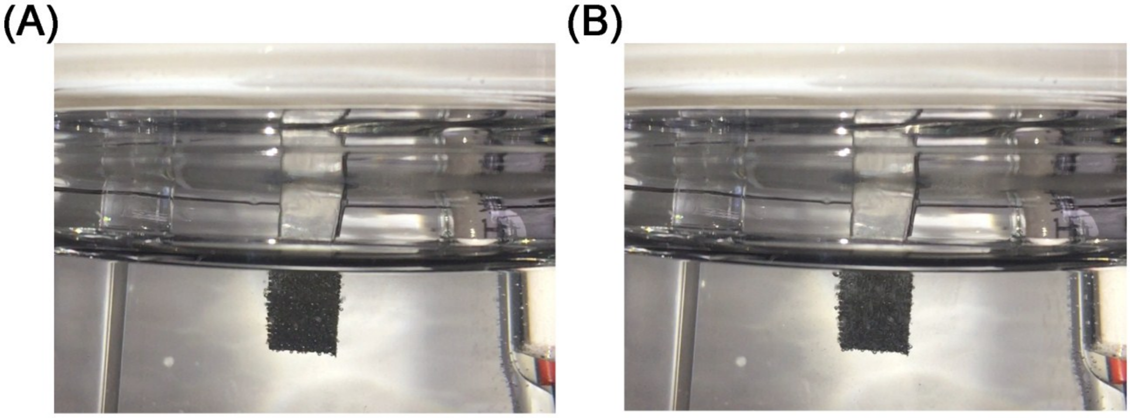

Fig. S9 The images of H_2 evolution process for Co_2P@C/CC at two fixed overpotentials of A) −100 and B) −150 mV, respectively.

Table S1. Comparison of HER performance of Co$_2$P@C/CC with that of representative non-noble-metal catalysts in acid electrolyte.

catalyst	onset overpotential (mV)	Tafel slope (mV dec^{-1})	current density (j, mA cm^{-2})	overpotential at corresponding j (mV)	exchange current density (mA cm^{-2})	ref.
hierarchical Mo$_2$C nanotubes	-82	62	10	172	0.017	[1]
			20	197		
MoS$_2$ microflake		63	10	174	0.019	[2]
CoSe$_2$ NP/ carbon fiber paper		42.1	10	137	0.0049	[3]
			100	181		
MoP		50	10	117	0.05	[4]
Co$_2$P	-70	71	10	134		[5]
			20	167		
CoP/Ti foil		50	10	75	0.14	[6]
CoP/CC	38	51	10	67	0.288	[7]
			100	204		
Mn$_{0.05}$Co$_{0.95}$Se$_2$		36			0.068	[8]
MoO$_x$/MoS$_2$ nanowires	-100	50	22	-400	0.045	[9]
hierarchical flower-like MoS$_2$@MoP-800	29	76	10	108		[10]
Mo-based Ni-MOF (HC800)		98	10	192		[11]
MoC-Mo$_2$C-31.4	38	43	10	126	0.011	[12]
Co-NRCNTs	-50	69	10	260	0.01	[13]
CoP nanocrystals	40	54	10	122	0.13	[14]
MoP@PC	77	66	10	153	0.21	[15]
CoNi@NC		105	10	142		[16]
Co$_2$P/Ti		45	10	95		[17]
Co$_2$P@N, P-PCN/CNTs		45	10	126		[18]
Co$_2$P/C	-20	50	10	125		[19]
			20	140		
CoP$_2$/RGO		51	10	70		[20]
MoP/RGO		58	20	118	0.201	[21]
MoS$_2$/G-20	30	67.4	10	110	0.14	[22]
Co$_2$P@C/CC	42	40.8	10	103	0.29	This work
			100	179		

Supplementary references

1. F. X. Ma, H. B. Wu, B. Y. Xia, C. Y. Xu and X. W. Lou, *Angew. Chem. Int. Ed.*, 2015, **54**, 15395.
2. D. Kiriya, P. Lobaccaro, H. Y. Nyein, P. Taheri, M. Hettick, H. Shiraki, C. M. Sutter-Fella, P. Zhao, W. Gao, R. Maboudian, J. W. Ager and A. Javey, *Nano lett.*, 2016, **16**, 4047.
3. D. Kong, H. Wang, Z. Lu and Y. Cui, *J. Am. Chem. Soc.*, 2014, **136**, 4897.
4. J. Kibsgaard and T. F. Jaramillo, *Angew. Chem. Int. Ed.*, 2014, **53**, 14433.
5. Z. Huang, Z. Chen, Z. Chen, C. Lv, M. G. Humphrey and C. Zhang, *Nano Energy*, 2014, **9**, 373.
6. 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.
7. J. Tian, Q. Liu, A. M. Asiri and X. Sun, *J. Am. Chem. Soc.*, 2014, **136**, 7587.
8. Y. Liu, X. Hua, C. Xiao, T. Zhou, P. Huang, Z. Guo, B. Pan and Y. Xie, *J. Am. Chem. Soc.*, 2016, **138**, 5087.
9. D. R. Cummins, U. Martinez, A. Sherehiy, R. Kappera, A. Martinez-Garcia, R. K. Schulze, J. Jasinski, J. Zhang, R. K. Gupta, J. Lou, M. Chhowalla, G. Sumanasekera, A. D. Mohite, M. K. Sunkara and G. Gupta, *Nat. commun.,* 2016, DOI: 10.1038/ncomms11857.
10. A. Wu, C. Tian, H. Yan, Y. Jiao, Q. Yan, G. Yang and H. Fu, *Nanoscale*, 2016, **8**, 11052.
11. X. Xu, F. Nosheen and X. Wang, *Chem. Mater.*, 2016, **28**, 6313.
12. H. Lin, Z. Shi, S. He, X. Yu, S. Wang, Q. Gao and Y. Tang, *Chem. Sci.*, 2016, **7**, 3399.
13. X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmekova and T. Asefa, *Angew. Chem. Int. Ed.*, 2014, **53**, 4372.
14. Q. Liu, J. Tian, W. Cui, P. Jiang, N. Cheng, A. M. Asiri and X. Sun, *Angew. Chem. Int. Ed.*, 2014, **53**, 6710.
15. J. Yang, F. Zhang, X. Wang, D. He, G. Wu, Q. Yang, X. Hong, Y. Wu and Y. Li, *Angew. Chem. Int. Ed.*, 2016, **55**, 12854.
16. J. Deng, P. Ren, D. Deng and X. Bao, *Angew. Chem. Int. Ed.*, 2015, **54**, 2100.
17. J. F. Callejas, C. G. Read, E. J. Popczun, J. M. McEnaney and R. E. Schaak, *Chem. Mater.*, 2015, **27**, 3769.
18. X. Z. Li, Y. Y. Fang, F. Li, M. Tian, X. F. Long, J. Jin, J. T. Ma, *J. Mater. Chem. A*, 2016, **4**, 15501
19. A. Dutta, A. K. Samantara, S. K. Dutta, B. K. Jena, N. Pradhan, *ACS Energy Lett.*, 2016, **1**, 169.
20 J. Wang, W. Yang and J. Liu, *J. Mater. Chem. A*, 2016, **4**, 4686.
21. G. Zhang, G. Wang, Y. Liu, H. Liu, J. Qu and J. Li, *J. Am. Chem. Soc.*, 2016, DOI: 10.1021/jacs.6b08491.
22. L. Ma, Y. Hu, G. Zhu, R. Chen, T. Chen, H. Lu, Y. Wang, J. Liang, H. Liu, C. Yan, Z. Tie, Z. Jin and J. Liu, *Chem. Mater.*, 2016, **28**, 5733.