## **Supporting Information for**

### Engineering a Nanotubular Mesoporous Cobalt Phosphide Electrocatalyst by

### Kirkendall Effect towards Highly Efficient Hydrogen Evolution Reaction

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Fig. S1 Photographs of  $Co_3O_4$ -NTs (a), W-Co<sub>3</sub>O<sub>4</sub>-NTs (b) and  $Co_3O_4$ -NPs (c).



Fig. S2 (a) Transmission electron microscopy (TEM) and (b) high-resolution TEM images of  $Co_3O_4$ -NTs.



**Fig. S3** (a) The field emission scanning electron microscopy image and the corresponding energy dispersive X-ray spectroscopy elemental mappings of CoP-NTs: (b) Co, (c) P.



**Fig. S4** Nyquist plots of CoP-NPs, W-CoP-NTs and CoP-NTs. Inset: the magnified high-frequency region of the corresponding plots.



**Fig. S5** (a) Nitrogen adsorption-desorption isotherms and (b) the corresponding pore size distribution plots of CoP-NPs, W-CoP-NTs and CoP-NTs.



**Fig. S6** X-ray diffraction patterns of Co<sub>3</sub>O<sub>4</sub>-NTs, CoP-NTs-2, CoP-NTs-5, CoP-NTs-8 and CoP-NTs-11, respectively.

Catalyst	Loading	Onset	Tafel slope ( <i>b</i> , mV dec <sup>-1</sup> )	Current density ( <i>j</i> , mA cm <sup>-2</sup> )	η at the	
	mass	overpotential			corresponding <i>j</i>	References
	(mg cm <sup>-2</sup> )	(η, mV vs. RHE)			(mV vs. RHE)	
CoP nanoparticles	2	~	50	20	85	1
CoP@C nanocables	0.35	140	61	10	170	2
$Co_{0.6}Mo_{1.4}N_2bulk$	0.24	~	~	10	200	3
CoSe <sub>2</sub> nanowire/carbon cloth	1.3	85	32	10	130	4
CoS <sub>2</sub> nanowire	1.7	75	51.6	10	145	5
Co/nitrogen-rich CNTs	0.28	50	69	10	260	6
CoS2-MoS2/CNTs	0.35	70	67	80	250	7
Co <sub>9</sub> S <sub>8</sub> @MoS <sub>2</sub> /CNFs	0.212	64	110	10	190	8
Co-Te-Se nanocompound	0.42	169	42	10	217	9
FeP nanosheets	0.28	100	67	10	240	10
MoP nanoparticles	0.071	100	60	~	~	11
MoP nanosheet/carbon cloth	2.5	50	58	>10	124	12
Ni <sub>2</sub> P nanosheet/Ni foam	3.5	80	68	15	120	13
WP <sub>2</sub> submicroparticles	0.5	54	57	10	161	14
CoP-NTs	0.35	53	50	10	152	This work

# Table. S1 Comparisons of the hydrogen evolution reaction performance for

representative Co-based composites and other metal phosphide catalysts.

**Notes:** <sup>*a*</sup> CNTs represent carbon nanotubes; <sup>*b*</sup> CNFs represent carbon nanofibers.

#### References

- E. J. Popczun, C. G. Read, C. W. Roske, N. S. Lewis and R. E. Schaak, *Angew. Chem. Int. Ed.*, 2014, 53, 5427-5430.
- 2 C. D. Wang, J. Jiang, X. L. Zhou, W. L. Wang, J. Zuo and Q. Yang, J. Power Sources, 2015, 286, 464-469.
- 3 B. Cao, G. M. Veith, J. C. Neuefeind, R. R. Adzic and P. G.Khalifah, J. Am. Chem. Soc., 2013, 135, 19186-19192.
- 4 Q. Liu, J. L. Shi, J. M. Hu, A. M. Asiri, Y. L. Luo and X. P. Sun, *ACS Appl. Mater*. *Interfaces*, 2015, **7**, 3877-3881.
- 5 M. S. Faber, R. Dziedzic, M. A. Lukowski, N. S. Kaiser, Q. Ding and S. Jin, *J. Am. Chem. Soc.*, 2014, **136**, 10053-10061.
- 6 X. Zou, X. Huang, A. Goswami, R. Silva, B. R. Sathe, E. Mikmeková and T. Asefa, Angew. Chem. Int. Ed., 2014, 53, 4372-4376.
- 7 Y. R. Liu, W. H. Hu, X. Li, B. Dong, X. Shang, G. Q. Han, Y. M. Chai, Y. Q. Liu and C. G. Liu, *Appl. Surf. Sci.*, 2016, **384**, 51-57.
- 8 H. Zhu, J. F. Zhang, R. P. Yanzhang, M. L. Du, Q. F. Wang, G. H. Gao, J. D. Wu,
  G. M. Wu, M. Zhang, B. Liu, J. M. Yao and X. W. Zhang, *Adv. Mater.*, 2015, 27, 4752-4759.
- 9 Y. P. Tian, Z. H. Zhang and Y. Q. Miao, J. Electrochem. Soc., 2016, 163, H625-H629.
- 10 Y. Xu, R. Wu, J. F. Zhang, Y. M. Shi and B. Zhang, *Chem. Commun.*, 2013, 49, 6656-6658.

- 11 X. B. Chen, D. Z. Wang, Z. P. Wang, P. Zhou, Z. Z. Wu and F. Jiang, *Chem. Commun.*, 2014, **50**, 11683-11685.
- 12 Z. H. Pu, S. Y. Wei, Z. B. Chen and S. C.Mu, Appl. Catal., B, 2016, 196, 193-198.
- 13 Y. M. Shi, Y. Xu, S. F. Zhuo, J. F. Zhang and B. Zhang, ACS Appl. Mater. Interfaces, 2015, 7, 2376-2384.
- 14 Z. C. Xing, Q. Liu, A. M. Asiri and X. P. Sun, ACS Catal., 2015, 5, 145-149.