Electronic supplementary information

Stable Zn electrodes enabled by an ultra-thin Zn phosphate protective layer

Jing Li,[a] Zhi Zheng,[a] Zixun Yu,[a] Fangxin She,[a] Leo Lai,[a] Justin Prabowo,[a] Wei Lv,[b,] Li Wei[a,*] and Yuan Chen[a,*]*

[a.] School of Chemical and Biomolecular Engineering, The University of Sydney, Darlington, NSW 2006, Australia

[b.] Institute of Materials Research, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, China.

Corresponding Authors:

lv.wei@sz.tsinghua.edu.cn (W.L.); l.wei@sydney.edu.au (L.W.); yuan.chen@sydney.edu.au (Y.C.)

Optimization of protective layer thickness

Zn foils were treated in PPA solutions at different concentrations (1, 5, and 20 wt.%). The resulting Zn foils were denoted as 1wt% PPA-Zn, 5wt% PPA-Zn, and 20wt% PPA-Zn, respectively. Next, symmetric cells were assembled to compare their internal resistance. As shown in Figure S1, the charge transfer resistance increases with the PPA concentration, suggesting that excessive Zn phosphate protective layers are detrimental to long-term cycling stability. Furthermore, at the current density of 5 mA cm^{-2} and the areal capacity of 1 mAh cm^{-2}, the symmetric cell with 5wt% PPA-Zn anode delivered the highest cycle stability (Figure S2). Therefore, we set the concentration of the PPA solution to 5 wt.% for the rest of our studies.

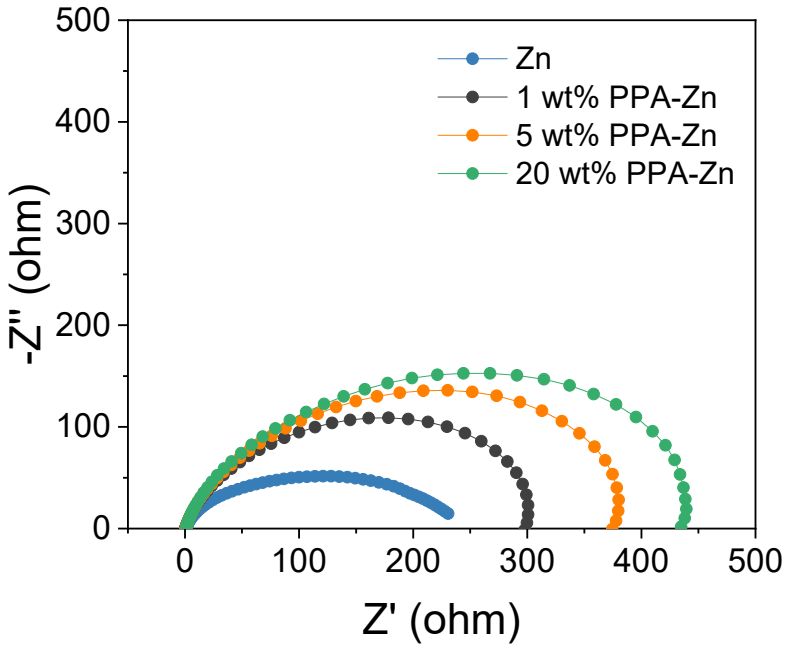

Figure S1. EIS profiles of symmetric cells assembled using Zn foils with Zn phosphate protective layers in different thicknesses: bare Zn, 1wt% PPA-Zn, 5wt% PPA-Zn, and 20wt% PPA-Zn.

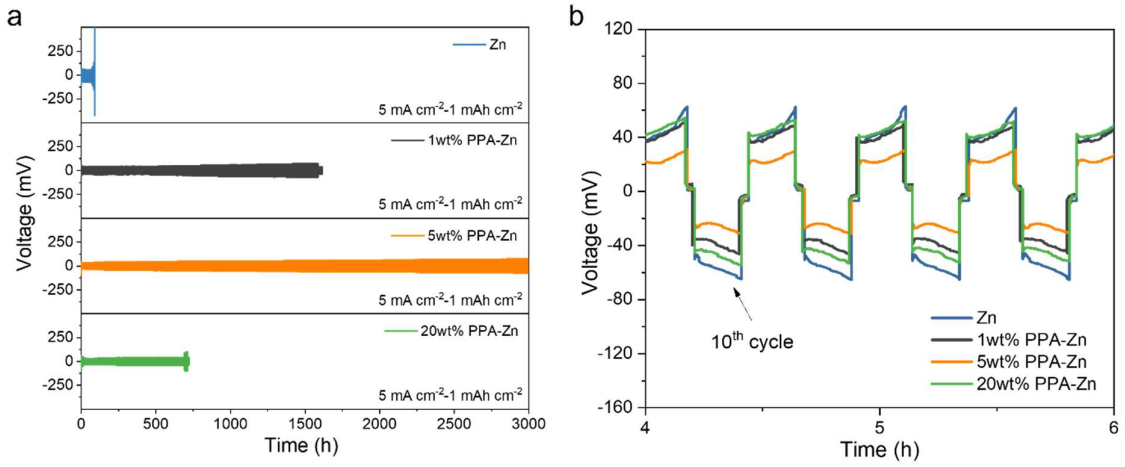

Figure S2. (a) Cycle stability and (b) voltage profiles of symmetric cells assembled using Zn foils with Zn phosphate protective layers in different thicknesses: bare Zn, 1wt% PPA-Zn, 5wt% PPA-Zn, and 20wt% PPA-Zn.

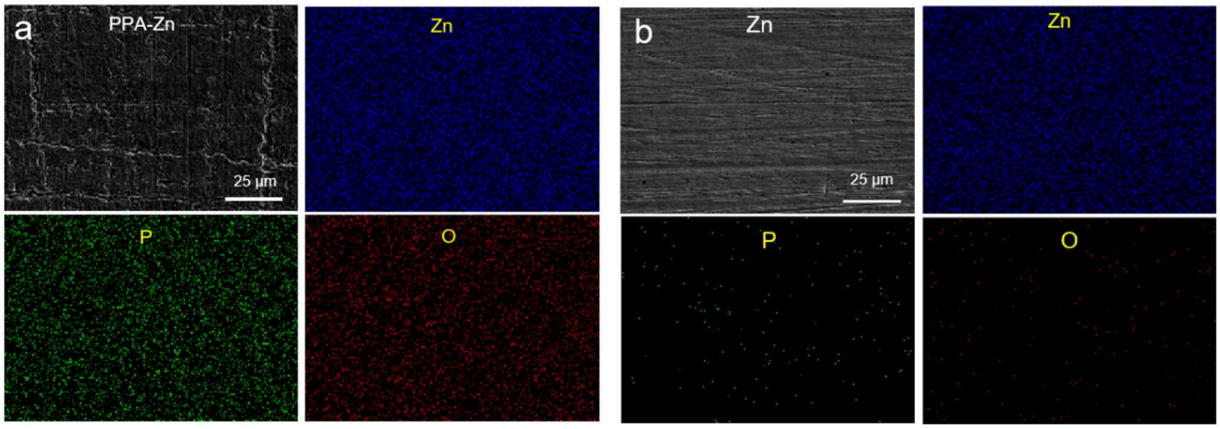

Figure S3. Element mapping results obtained by SEM-EDX for (a) PPA-Zn and (b) Zn

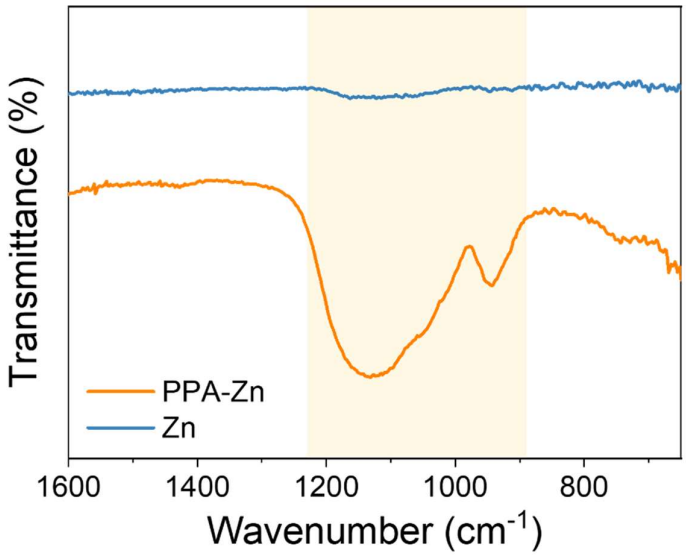

Figure S4. FTIR spectra of PPA-Zn and Zn foil.

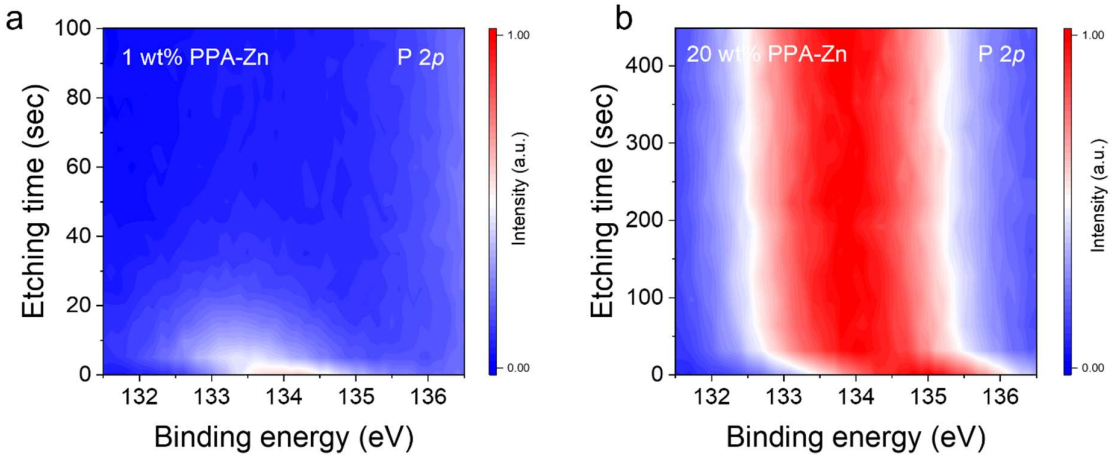

Figure S5. The XPS depth profile of P 2*p* for (a) 1 wt% PPA-Zn and (b) 20 wt% PPA-Zn.

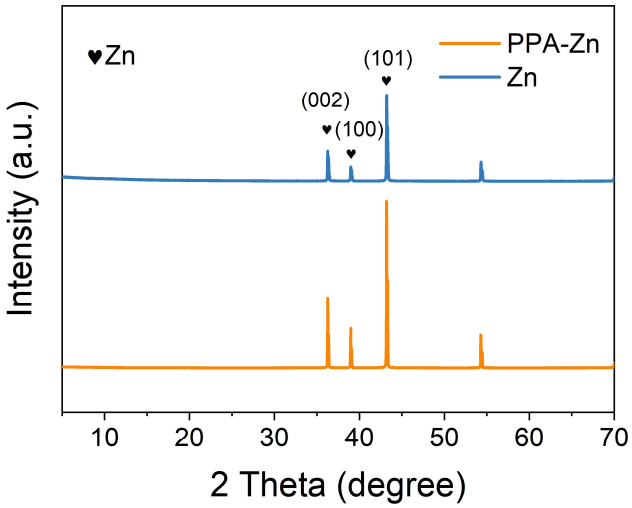

Figure S6. XRD patterns of PPA-Zn and Zn foil.

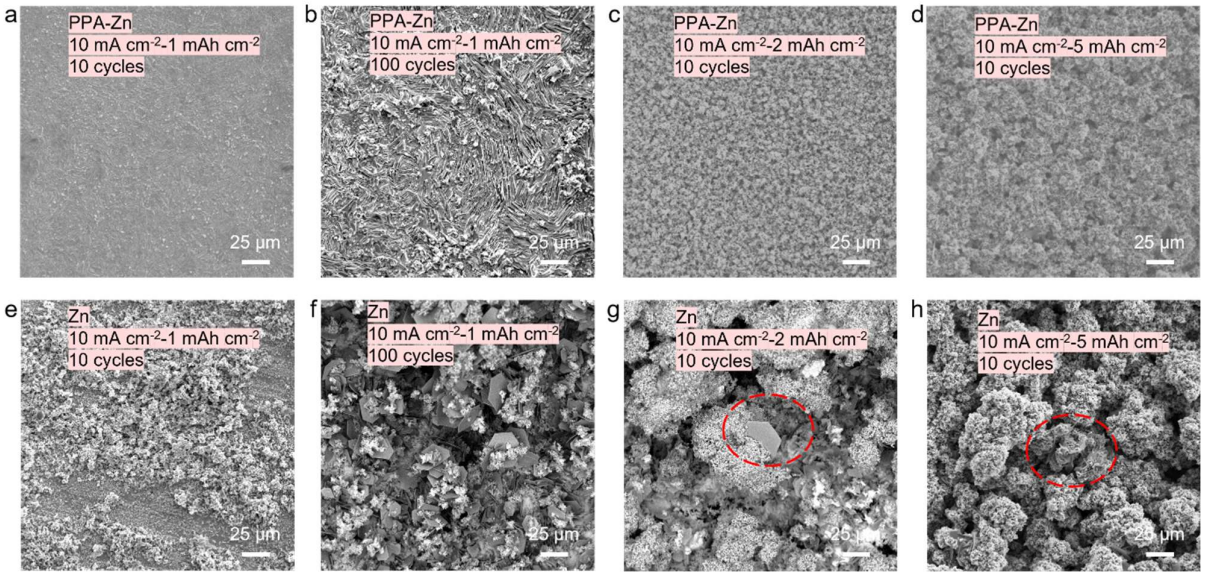

Figure S7. SEM images of PPA-Zn foils after plating Zn at different current densities, areal capacities, and charge/discharge cycles: (a) 10 charge/discharge cycles and (b) 100 charge/discharge cycles at the current density of 10 mA cm^{-2} and the areal capacity of 1 mAh cm^{-2} , (c) 10 charge/discharge cycles at the current density of 10 mA cm^{-2} and the areal capacity of 2 mAh cm^{-2}, (d) 10 charge/discharge cycles at the current density of 10 mA cm^{-2} and the areal capacity of 5 mAh cm^{-2}. SEM images of pristine Zn foils after plating Zn at different current densities, areal capacities, and cycles: (e) 10 charge/discharge cycles and (f) 100 charge/discharge cycles at the current density of 10 mA cm^{-2} and the areal capacity of 1 mAh cm^{-2} , (g) 10 charge/discharge cycles at the current density of 10 mA cm^{-2} and the areal capacity of 2 mAh cm^{-2}, (h) 10 cycles at the current density of 10 mA cm^{-2} and the areal capacity of 5 mAh cm^{-2}.

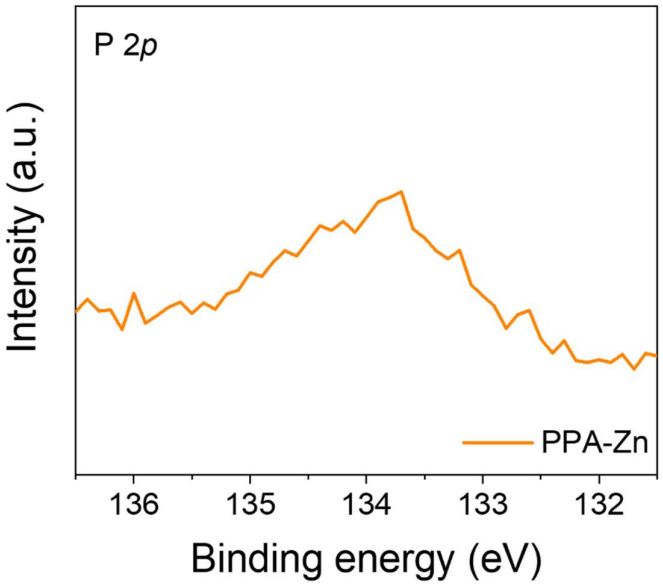

Figure S8. XPS spectrum of PPA-Zn after Zn plating at the current density of 10 mA cm^{-2} and areal capacity of 1 mAh cm^{-2}.

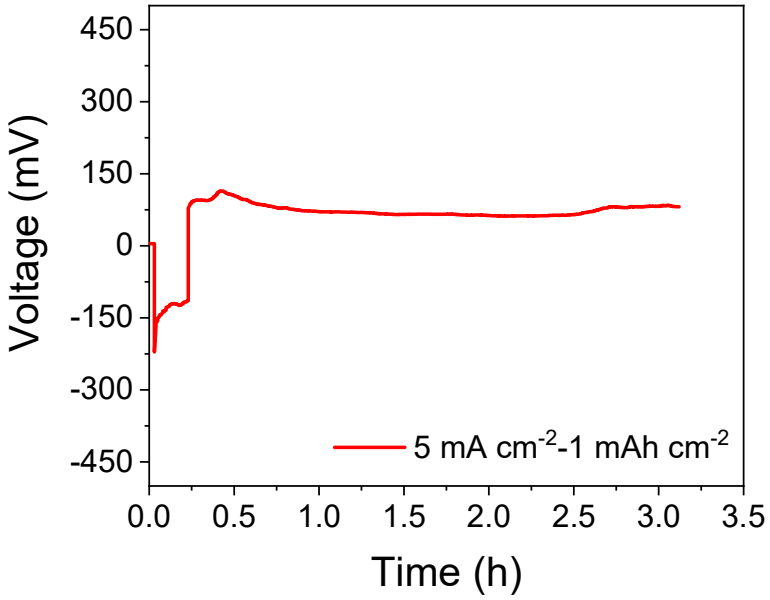

Figure S9. The discharge-charge curve of a symmetric cell assembled using PPA-Zn. Because there is Zn at the initial stage, the cut-off voltage cannot reach 0.5 V.

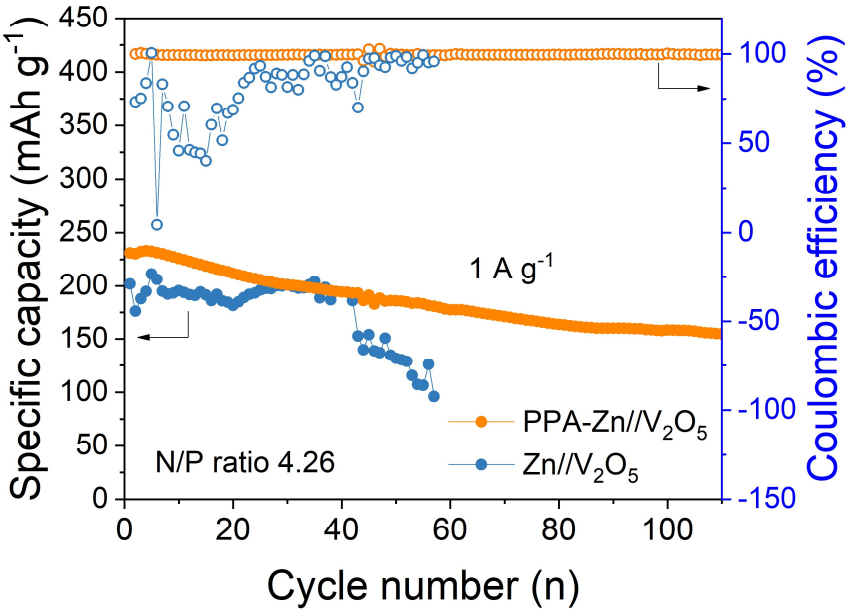

Figure S10. The cycle stability of PPA-Zn//V_2O_5 and the Zn//V_2O_5 full cells.

Table S1. Comparison of the electrochemical performance of Zn metal-based symmetric cells reported in recently published studies. For the studies in which the DODs were not mentioned, we calculated the DODs according to their supplied information and marked as C.

Anode	Coating thickness	Volume increment after coating	Current density (mA cm^{-2})	Areal Capacity (mAh cm^{-2})	DOD	Cycle Life (h)	Cumulative plating capacity (Ah cm^{-2})	Reference
PPA-Zn	**45 nm**	**0.09%**	**2**	**1**	**3.4%**	**6500**	**6.5**	**This work**
PPA-Zn	**45 nm**	**0.09%**	**10**	**5**	**17.0%**	**300**	**1.5**	**This work**
MOF@Zn	8-10 μm	/	3	0.5	/	500	0.75	*ACS Appl. Mater. Interfaces*, **2019**, 11, 32046[1]
rGO@Zn	/	/	10	2	C 3.1%	200	1.00	*ACS Appl. Mater. Interfaces*, **2018**, 10, 25446[2]
TiN@Zn	1.3 μm	0.65%	2	2	C 1.7%	1000	1	*ACS Energy Lett.*, **2022**, 7, 197[3]
ZnS@Zn	0.5 μm	5%	2	2	C 34.2%	1100	1.10	*Adv. Mater.*, **2020**, 32, 2003021[4]
$Zn_3(PO_4)_2$@Zn	140 nm	1.4%/ 0.2%	1	5	C 14.2%	800	0.40	*Adv. Mater.*, **2021**, 33, 2007416[5]
Zn@CNT	/	/	5	2.5	C 37.5%	100	0.25	*Adv. Mater.*, **2019**, 31, 1903675[6]
Zn@3D-CNT/EVA	/	/	10	1	/	100	0.50	*Adv. Mater.*, **2022**, 34, 2200860[7]
$CaCO_3$@Zn	/	/	0.25	0.05	/	400	0.05	*Adv. Energy Mater.*, **2018**, 8, 1801090[8]
Zn@3D-Ni	/	/	5	2	/	200	0.50	*Adv. Energy Mater.*, **2021**, 11, 2003927 [9]
Kaolin@Zn	21 μm	1%	4.4	1.1	C 1.9%	800	1.76	*Adv. Funct. Mater.*, **2020**, 30, 2000599[10]
PVB@Zn	1 μm	10%	0.5	0.5	C	2200	0.55	*Adv. Funct. Mater.*, **2020**, 30, 2001263[11]

					8.5%			
$NaTi_2(PO_4)_3$@Zn	10-25 μm	/	1	1	/	250	0.13	*Adv. Funct. Mater.*, **2020**,30, 2004885[12]
TiO_2+PVDF@Zn	5 μm	6.25%	8.85	8.85	60%	250	1.11	*Adv. Funct. Mater.*, **2020**, 30, 2001867[13]
Zn@ZnO	//	/	5	2.5	4.3%	100	0.25	*Adv. Funct. Mater.*, **2020**, 30, 2004210[14]
ZrO2@Zn	4 μm	/	5	1	/	2100	5.25	*Adv. Funct. Mater.*, **2020**, 13, 1908528[15]
Mxene@Zn	200 nm	0.4%	0.2	0.2	C 0.68%	850	0.09	*Angew. Chem. Int. Ed.*, 2021, 60, 2861[16]
CNT@Zn	/	/	1	1	/	400	0.20	*Chem. Eng. J.*, **2020**, 384, 123355[17]
In@Zn	8 μm	8%	4	1	C 1.7%	400	0.80	*Chem. Eng. J.*, **2020**, 396, 125363[18]
Zn@Graphite fiber	/	/	1	1	C 16.7%	700	0.35	*Electrochim. Acta*, **2017**, 244, 172[19]
Zn@ZnO-3D	/	/	5	1.25	1.3%	500	1.25	*Energy Environ. Sci.*, **2020**, 13, 503[20]
PA@ Zn	40 μm	200%/ 28.6%	10	10	85%	75	0.38	*Energy Environ. Sci.*, **2019**, 12, 1938[21]
3D-gradient alloy	/	/	3	3	/	700	1.05	*Energy Environ. Sci.*, **2022**, 15, 1086[22]
Cu–Zn/Zn	132.2 μm	/	1	0.5	/	1500	0.75	*Energy Stor. Mater.*, **2020**, 27, 205[23]
3D porous Zn	/	/	5	10	71%	200	0.50	*Energy Stor. Mater.*, **2020**, 30, 104[24]
C sphere@Zn	3.9 μm	3.9%	1	1	C 1.7%	1000	0.50	*Energy Stor. Mater.*, **2020**, 25, 858[25]
Zn@MOF	/	/	1	1	C 20%	50	0.03	*Joule*, **2019**, 3, 1289[26]
Al_2O_3@Zn	10 nm	/	1	1	C 0.85%	500	0.25	*J. Mater. Chem. A*, **2020**, 8,7836[27]

Liquid metal@Zn	1 mm	/	2.5	2.5	/	200	0.25	*J. Mater. Chem. A*, **2021**, 9, 5597[28]
$AgZn_3$@Zn	14 μm	/	0.25	0.5	/	1750	0.218	*J. Mater. Chem. A*, **2021**, 9,8452[29]
Montmorillonite @Zn	/	/	2	1	C 5.7%	700	0.7	*J. Mater. Chem. A*, **2021**, 9,16814[30]
TiO_2@Zn	20 μm	66.7%	2	2	C 11.4%	280	0.28	*Nature Commun.*, **2020**, 11, 3961[31]
Zn@3D In	/	/	1	1	/	1000	0.50	*Nano Energy*, **2022**, 99, 107331 [32]

References cited in the ESI

1. M. Liu, L. Yang, H. Liu, A. Amine, Q. Zhao, Y. Song, J. Yang, K. Wang and F. Pan, *ACS Appl. Mater. Interfaces*, 2019, **11**, 32046-32051.
2. C. Shen, X. Li, N. Li, K. Xie, J. G. Wang, X. Liu and B. Wei, *ACS Appl. Mater. Interfaces*, 2018, **10**, 25446-25453.
3. J. Zheng, Z. Cao, F. Ming, H. Liang, Z. Qi, W. Liu, C. Xia, C. Chen, L. Cavallo, Z. Wang and H. N. Alshareef, *ACS Energy Lett.*, 2021, **7**, 197-203.
4. J. Hao, B. Li, X. Li, X. Zeng, S. Zhang, F. Yang, S. Liu, D. Li, C. Wu and Z. Guo, *Adv. Mater.*, 2020, **32**, 2003021.
5. X. Zeng, J. Mao, J. Hao, J. Liu, S. Liu, Z. Wang, Y. Wang, S. Zhang, T. Zheng, J. Liu, P. Rao and Z. Guo, *Adv. Mater.*, 2021, **33**, e2007416.
6. Y. Zeng, X. Zhang, R. Qin, X. Liu, P. Fang, D. Zheng, Y. Tong and X. Lu, *Adv. Mater.*, 2019, **31**, 1903675.
7. M. Zhang, P. Yu, K. Xiong, Y. Wang, Y. Liu and Y. Liang, *Adv. Mater.*, 2022, **34**, e2200860.
8. L. Kang, M. Cui, F. Jiang, Y. Gao, H. Luo, J. Liu, W. Liang and C. Zhi, *Adv. Energy Mater.*, 2018, **8**, 1801090.
9. G. Zhang, X. Zhang, H. Liu, J. Li, Y. Chen and H. Duan, *Adv. Energy Mater.*, 2021, **11**, 2003927.
10. C. B. Deng, X. S. Xie, J. W. Han, Y. Tang, J. W. Gao, C. X. Liu, X. D. Shi, J. Zhou and S. Q. Liang, *Adv. Funct. Mater.*, 2020, **30**, 2000599.
11. J. Hao, X. Li, S. Zhang, F. Yang, X. Zeng, S. Zhang, G. Bo, C. Wang and Z. Guo, *Adv. Funct. Mater.*, 2020, **30**, 2001263.
12. M. Liu, J. Cai, H. Ao, Z. Hou, Y. Zhu and Y. Qian, *Adv. Funct. Mater.*, 2020, **30**, 2004885.
13. R. Zhao, Y. Yang, G. Liu, R. Zhu, J. Huang, Z. Chen, Z. Gao, X. Chen and L. Qie, *Adv. Funct. Mater.*, 2020, **31**, 2001867.
14. J. Y. Kim, G. Liu, G. Y. Shim, H. Kim and J. K. Lee, *Adv. Funct. Mater.*, 2020, **30**, 2004210.
15. P. Liang, J. Yi, X. Liu, K. Wu, Z. Wang, J. Cui, Y. Liu, Y. Wang, Y. Xia and J. Zhang, *Adv. Funct. Mater.*, 2020, **30**, 1908528.
16. N. Zhang, S. Huang, Z. Yuan, J. Zhu, Z. Zhao and Z. Niu, *Angew. Chem. Int. Ed. Engl.*, 2021, **60**, 2861-2865.
17. L. B. Dong, W. Yang, W. Yang, H. Tian, Y. F. Huang, X. L. Wang, C. J. Xu, C. Y. Wang, F. Y. Kang and G. X. Wang, *Chem. Eng. J.*, 2020, **384**, 123355.
18. K. Hu, X. Guan, R. Lv, G. Li, Z. Hu, L. Ren, A. Wang, X. Liu and J. Luo, *Chem. Eng. J.*, 2020, **396**, 125363.
19. L.-P. Wang, N.-W. Li, T.-S. Wang, Y.-X. Yin, Y.-G. Guo and C.-R. Wang, *Electrochim. Acta*, 2017, **244**, 172-177.
20. X. Xie, S. Liang, J. Gao, S. Guo, J. Guo, C. Wang, G. Xu, X. Wu, G. Chen and J. Zhou, *Energy Environ. Sci.*, 2020, **13**, 503-510.
21. Z. Zhao, J. Zhao, Z. Hu, J. Li, J. Li, Y. Zhang, C. Wang and G. Cui, *Energy Environ. Sci.*, 2019, **12**, 1938-1949.
22. G. J. Liang, J. X. Zhu, B. X. Yan, Q. Li, A. Chen, Z. Chen, X. Q. Wang, B. Xiong, J. Fan, J. Xu and C. Y. Zhi, *Energy Environ. Sci.*, 2022, **15**, 1086-1096.
23. Z. Cai, Y. Ou, J. Wang, R. Xiao, L. Fu, Z. Yuan, R. Zhan and Y. Sun, *Energy Storage Mater.*, 2020, **27**, 205-211.

24. W. Guo, Z. Cong, Z. Guo, C. Chang, X. Liang, Y. Liu, W. Hu and X. Pu, *Energy Storage Mater.*, 2020, **30**, 104-112.
25. P. Liu, W. Liu, Y. Huang, P. Li, J. Yan and K. Liu, *Energy Storage Mater.*, 2020, **25**, 858-865.
26. Z. Wang, J. Huang, Z. Guo, X. Dong, Y. Liu, Y. Wang and Y. Xia, *Joule*, 2019, **3**, 1289-1300.
27. H. He, H. Tong, X. Song, X. Song and J. Liu, *J. Mater. Chem. A*, 2020, **8**, 7836-7846.
28. H. Jia, Z. Wang, M. Dirican, S. Qiu, C. Y. Chan, S. Fu, B. Fei and X. Zhang, *J. Mater. Chem. A*, 2021, **9**, 5597-5605.
29. Y. Wang, Y. Chen, W. Liu, X. Ni, P. Qing, Q. Zhao, W. Wei, X. Ji, J. Ma and L. Chen, *J. Mater. Chem. A*, 2021, **9**, 8452-8461.
30. L. Hong, X. Wu, C. Ma, W. Huang, Y. Zhou, K.-X. Wang and J.-S. Chen, *J. Mater. Chem. A*, 2021, **9**, 16814-16823.
31. Q. Zhang, J. Luan, X. Huang, Q. Wang, D. Sun, Y. Tang, X. Ji and H. Wang, *Nat. Commun.*, 2020, **11**, 3961.
32. J. Yin, Y. Wang, Y. Zhu, J. Jin, C. Chen, Y. Yuan, Z. Bayhan, N. Salah, N. A. Alhebshi, W. Zhang, U. Schwingenschlögl and H. N. Alshareef, *Nano Energy*, 2022, **99**, 107331.