Electronic Supplementary Material (ESI) for Journal of Materials Chemistry A.

Supporting Information

Paragenesis BN/CNTs Hybrid as a Monoclinic Sulfur Host for High Rate and Ultralong Life Lithium-Sulfur Battery

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Table S1. The specific surface area and pore volume of polar materials used as sulfur host for lithium-sulfur batteries in the literature.

Host materials	S_{BET} (m^2 g^{-1})	V_{total} (cm^3 g^{-1})	Refs.
Co_4N	48.4	0.237	1
TiN	69.6	0.32	2
NbC	22.37	0.078	3
Co_3O_4 nanosheets	80.4		4
TiO_2 nanosheet	92	0.27	5
Co_3O_4 nanoneedle	75.6	0.26	6
SnO_2 shells	66.7		7
hollow TiO_2 sphere	76	0.15	8
TiO_2 nanotube	134.9		9
MoO_2	70	0.3	10
Rutile TiO_2	73.6	0.213	11
Co_3S_4	31		12
VN/C	38.9	0.084	13
C/TiO_2	148	0.29	14
$La_{0.6}Sr_{0.4}CoO_{3-\delta}$	70.3		15
CC/TiO_2	44.1		16
SnO_2	29	0.125	17
C/SnO_2 nanosheets	89.6		18
CNTs/MnO	51.3		19
$BaTiO_3$	12		20
p-BN/CNTs	168	0.33	This work

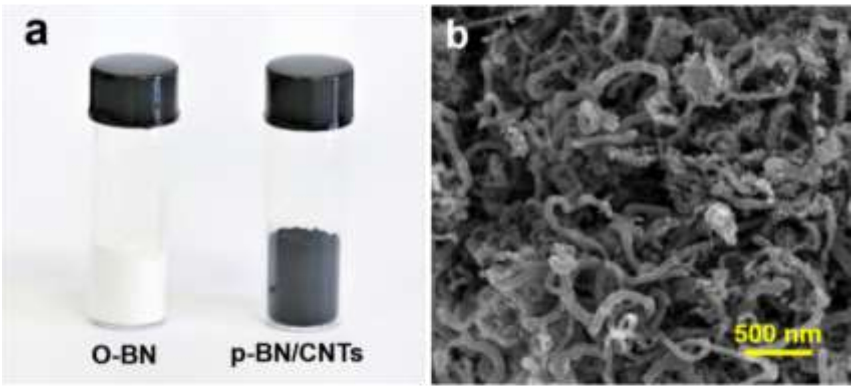

Figure S1. (a) The photograph of O-BN and p-BN/CNTs. (b) SEM image of p-BN/CNTs.

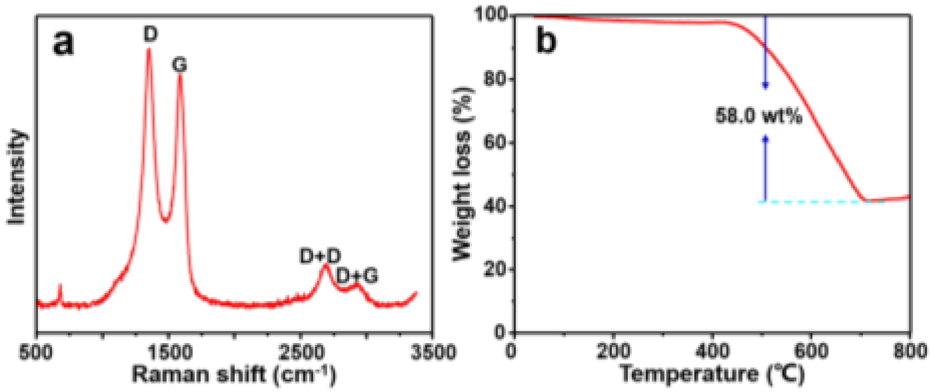

Figure S2. (a) Raman spectrum, (b) Thermogravimetric analysis of p-BN/CNTs.

Raman spectrum of p-BN/CNTs (**Figure S2**a) exhibits two intense peaks centered at approximately 1344 and 1582 cm^{-1} and two small peaks centered at approximately 2620 and 2900 cm^{-1}. The peak at 1582 cm^{-1} is generally observed in single crystalline graphite and attributed to the in-plane bond stretching of sp^2 C pairs. As the D peak of carbon and the peak assigned to E_{2g} vibration mode of BN are so close, thus the peak at 1344 cm^{-1} is maybe the superimposition of the above two peaks. The other peaks, located at ~2620 and 2900 cm^{-1}, are called 2D (D+D) and D+G bands and correspond to the second-order of Raman spectrum in overtone and combination modes, respectively.

The 58% weight loss of p-BN/CNTs at 400-700 °C is due to combustion of carbon nanotubes. The Co was oxidized into Co_3O_4 at the high temperature of 400-700 °C under air and 7.9 wt% Co can be generated 10.8 wt% Co_3O_4, thus the BN content is approximately 31.2 wt% (58%+10.8%+31.2%=100%).

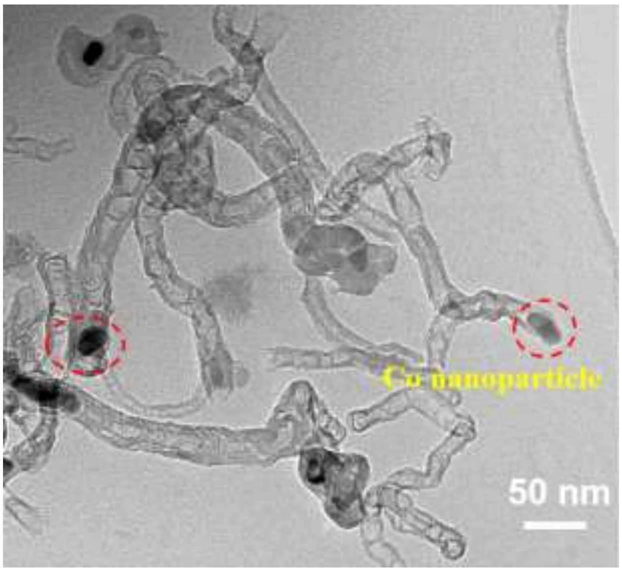

Figure S3. TEM images of p-BN/CNTs.

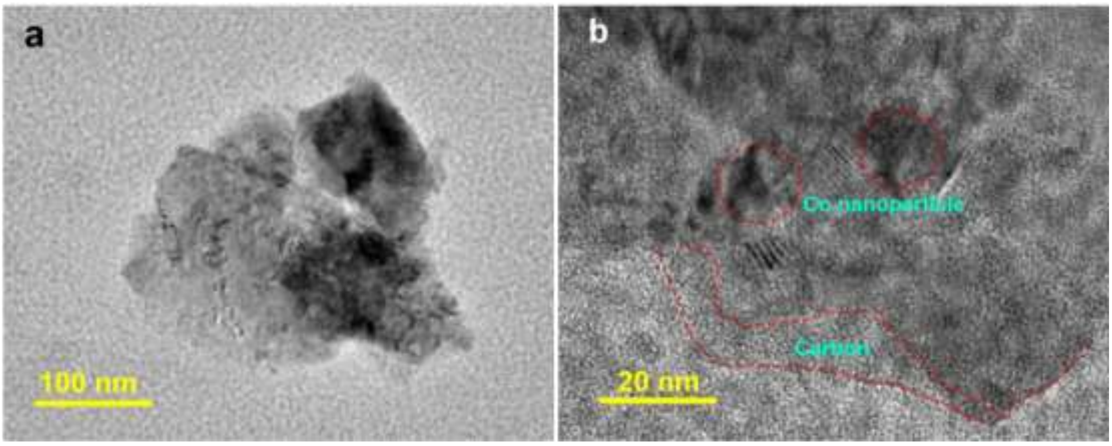

Figure S4. TEM images of control sample prepared without H_3BO_3

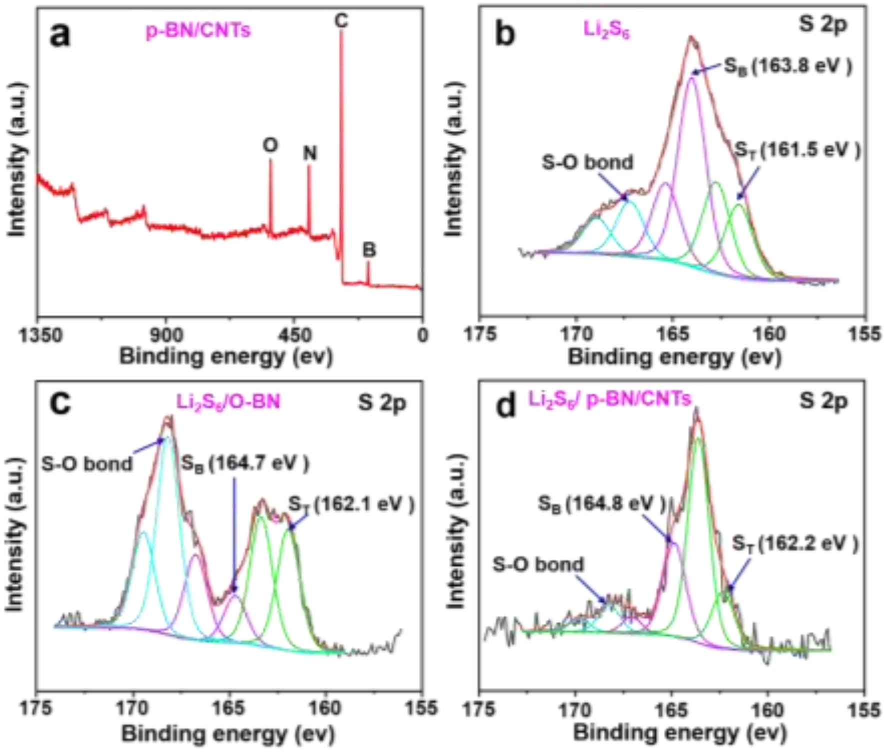

Figure S5. (a) XPS spectrum of p-BN/CNTs. (b-d) High-resolution XPS S 2p spectra of (b) Li_2S_6, (c) Li_2S_6/O-BN and (d) Li_2S_6/p-BN/CNTs.

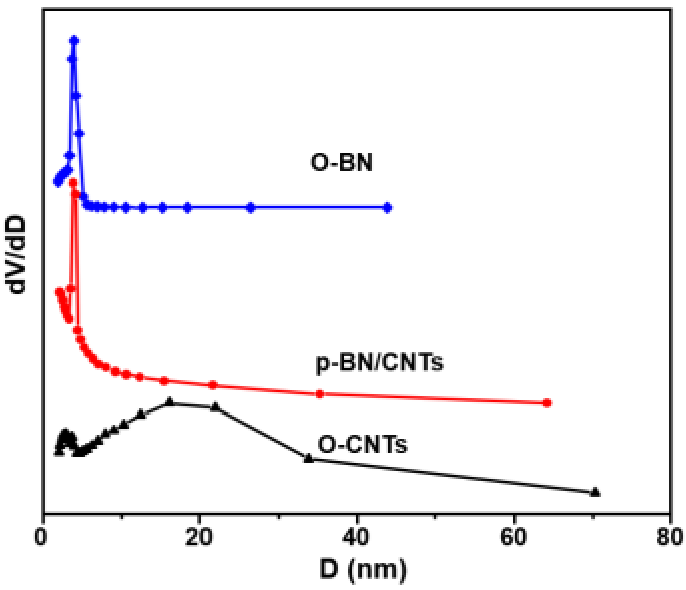

Figure S6. Pore size distributions of O-BN, p-BN/CNTs and O-CNTs.

Figure S7. Static adsorption test of O-CNTs, O-BN and p-BN/CNTs with Li_2S_6 solution.

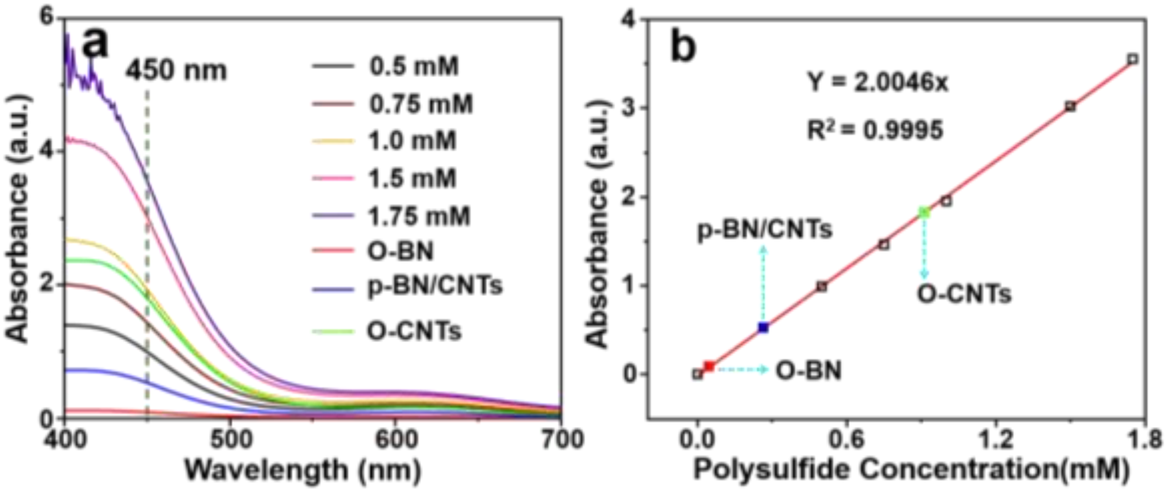

Figure S8. (a) UV/Vis-spectra of Li_2S_6 solution between 0.5 and 1.75 mM. (b) Linear calibration of the absorbance at 450 nm of Li_2S_6 solutions among 0.5 and 1.75 mM.

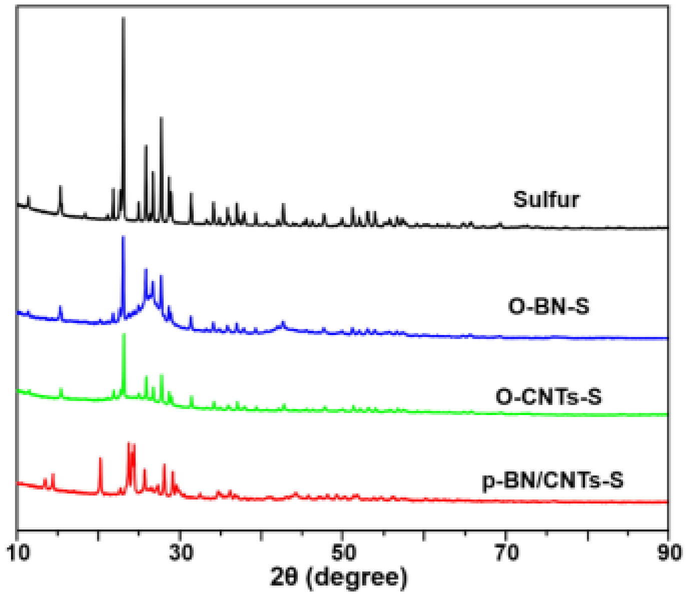

Figure S9. XRD patterns of p-BN/CNTs-S after storing it for two months, and sulfur, O-BN-S, O-CNTs.

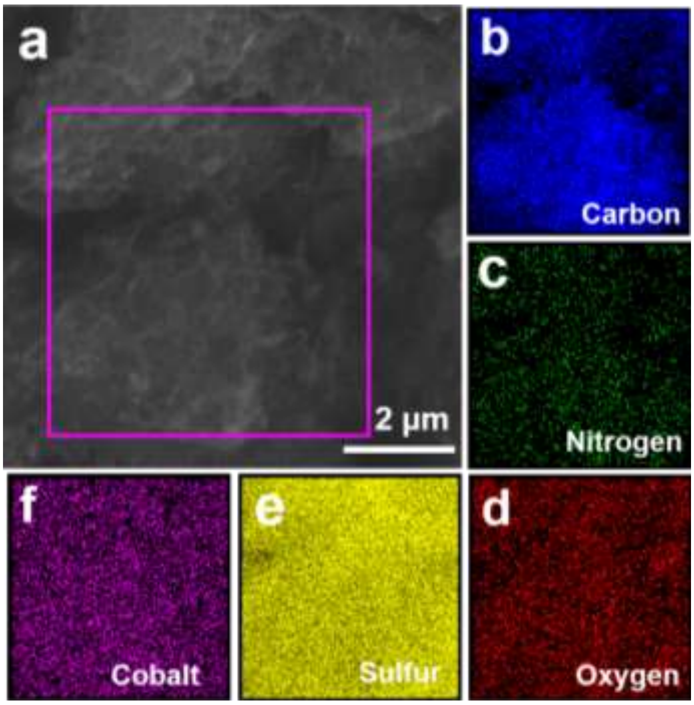

Figure S10. (a) SEM image and EDS mapping of p-BN/CNTs-S. (b-f) EDS elemental maps of (b) carbon, (c) nitrogen, (d) oxygen, (e) sulfur and (f) cobalt.

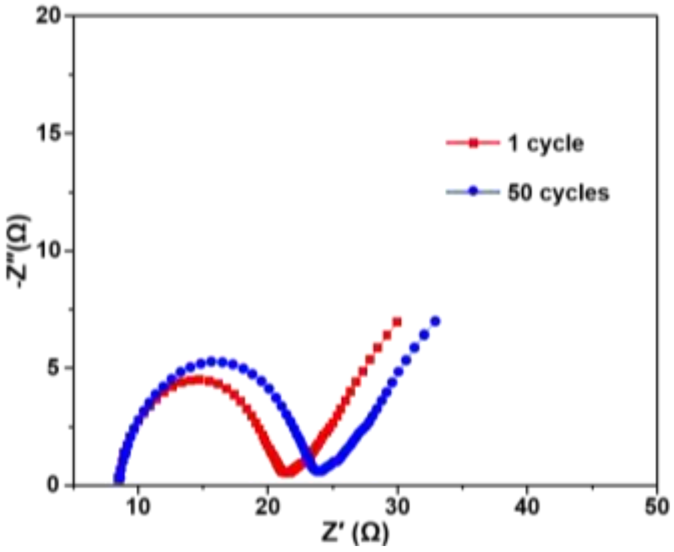

Figure S11. Electrochemical impedance spectra of p-BN/CNTs-S after the first cycle and 50 cycles.

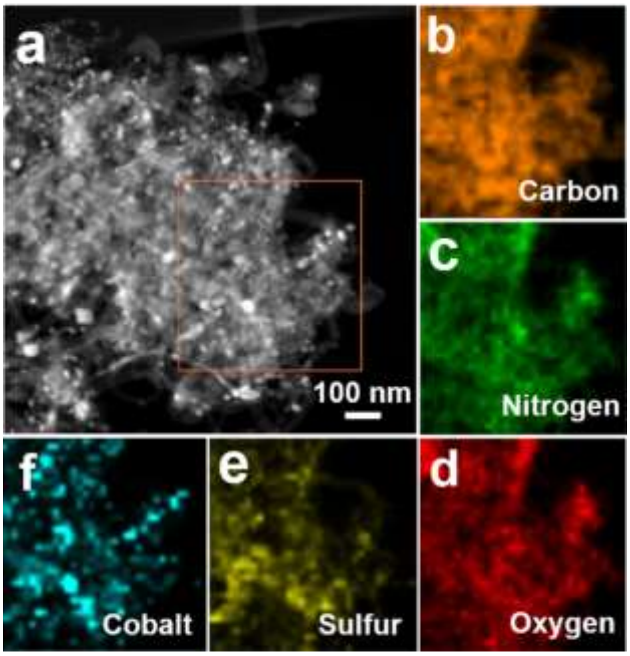

Figure S12. (a) STEM image and EDS elemental mapping of p-BN/CNTs-S after 50 cycles. (b-f) EDS elemental maps of (b) carbon, (c) nitrogen, (d) oxygen, (e) sulfur and (f) cobalt.

Table S2. The cycle and rate performances of the Li-S batteries in the literature

Materials	Sulfur content (%)	Sulfur loading (mg cm^{-2})	1 C			Rate performance	Refs.
			Cycle number	Last cycle (mAh g^{-1})	Decay rates (%)	Specific capacity (mAh g^{-1})	
p-BN/CNTs	66	1.5-2.0	500	816	0.045	840 (4C)	This work
Hollow Co_3S_4	53	2.5	450	610	0.08	752 (2C)	21
VN/graphene	56	3	200	917	0.0935	701 (3C)	22
CMK-3/polymer	48	1.0-1.5	100	838	0.3829	850 (3 C)	23
PCNTs@Gra/DTT	63	0.49	400	880	0.05	750 (3C)	24
Carbon/Celgard	70	0.7	200	721	0.20	450 (4 C)	25
Carbon Rods	78.9	0.93	300	700	0.0927	770 (3 C)	26
Polypyrrole-MnO_2	70	1.0~2.0	500	550	0.071	350 (4 C)	27
Carbon	70	0.9–1.2	250	588	0.1386	480 (3 C)	28
Graphene Oxide	70	1−1.2	400	750	0.08	800 (1 C)	29
Carbon	50.5		150	558	0.13	696.5 (1 C)	30
Co-N-GC	70	1.5-2.0	500	625	0.09	685 (2 C)	31
GN-CNT	76.4	1.3–1.6	500	476	0.09	535 (2 C)	32
Ti_4O_7	70	0.4-0.6				861 (2 C)	33
TiO-G	65	1.0				831 (2 C)	34
MoS_2	75	1.5				850 (2 C)	35
SnO/CNT	70	1.0–1.3				773 (3C)	36
MIL-100(V)/rGO	50	0.9–1.0				600 (0.5 C)	37
MoS_2/Celgard	65					770 (1 C)	38
Cobalt Hydroxide	75	3				500 (1 C)	39
Nb_2O_5	60	1.5				741 (3 C)	40
Carbon nanotubes	50					439 (2 C)	41
RGO–CNTs	73	1.1				712 (2 C)	42
Si/SiO_2 carbon	70					614 (2 C)	43
Cabon	68.3	1-1.5				738 (2 C)	44
Carbon nanotube	70	1.2				300 (4 C)	45
TiO_{2-x}	70	1.5				655 (2 C)	46
Carbon	70	1.3				900 (2 C)	47
CNT-Graphene	73	1.3–1.6				696 (2 C)	48
Ti_3C_2 Nanoribbon	68	0.7-1.0				403 (4 C)	49
$Ti_3C_2T_x$@Meso-C	72.8	2.0				544.3 (4 C)	50

References

1. D.-R. Deng, F. Xue, Y.-J. Jia, J.-C. Ye, C.-D. Bai, M.-S. Zheng and Q.-F. Dong, *ACS Nano*, 2017, **11**, 6031-6039.
2. Z. Cui, C. Zu, W. Zhou, A. Manthiram and J. B. Goodenough, *Adv. Mater.*, 2016, **28**, 6926-6931.
3. W. Cai, G. Li, K. Zhang, G. Xiao, C. Wang, K. Ye, Z. Chen, Y. Zhu and Y. Qian, *Adv. Funct. Mater.*, 2018, **28**, 1704865.
4. H. Wang, T. Zhou, Dan Li, H. Gao, G. Gao, A. Du, H. Liu and Z. Guo, *ACS Appl. Mater. Interfaces*, 2017, **9**, 4320-4325.
5. X. Yang, X. Qian, L. Jin, D. Zhao, S. Wang, D. Rao, S. Yao, X. Shen, Y. Zhou and X. Xi, *J. Solid State Electrochem.*, 2016, **20**, 2161-2168.
6. Z. Chang, H. Dou, B. Ding, J. Wang, Y. Wang, X. Hao and D. R. MacFarlane, *J. Mater. Chem. A*, 2017, **5**, 250-257.
7. L. P. Zhang, Y. F. Wang, S. Q. Gou and J. H. Zeng, *J. Phys. Chem. C*, 2015, **119**, 28721-28727.
8. J. Li, B. Ding, G. Xu, L. Hou, X. Zhang and C. Yuan, *Nanoscale*, 2013, **5**, 5743-5746.
9. K. Xie, Y. Han, W. Wei, H. Yu, C. Zhang, J.-G. Wang, W. Lu and B. Wei, *RSC Adv.*, 2015, **5**, 77348-77353.
10. Q. Qu, T. Gao, H. Zheng, Y. Wang, X. Li, X. Li, J. Chen, Y. Han, J. Shao and H. Zheng, *Adv. Mater. Interfaces*, 2015, **2**, 1500048.

11. Q. Sun, K. Chen, Y. Liu, Y. Li and M. Wei, *Chem. Eur. J.*, 2017, **23**, 16312-16318.
12. J. Pu, Z. Shen, J. Zheng, W. Wu, C. Zhu, Q. Zhou, H. Zhang and F. Pan, *Nano Energy*, 2017, **37**, 7-14.
13. X. Li, K. Ding, B. Gao, Q. Li, Y. Li, J. Fu, X. Zhang, P. K. Chu and K. Huo, *Nano Energy*, 2017, **40**, 655-662.
14. J. Yao, T. Mei, Z. Cui, Z. Yu, K. Xu and X. Wang, *Chem. Eng. J.*, 2017, **330**, 644-650.
15. Z. Hao, R. Zeng, L. Yuan, Q. Bing, J. Liu, J. Xiang and Y. Huang, *Nano Energy*, 2017, **40**, 360-368.
16. T. Lei, Y. Xie, X. Wang, S. Miao, J. Xiong and C. Yan, *Small*, 2017, **13**, 1701013.
17. J. Liu, L. Yuan, K. Yuan, Z. Li, Z. Hao, J. Xiang and Y. Huang, *Nanoscale*, 2016, **8**, 13638-13645.
18. M. Wang, L. Fan, X. Wu, D. Tian, J. Cheng, Y. Qiu, H. Wu, B. Guan, N. Zhang, K. Sun and Y. Wang, *J. Mater. Chem. A*, 2017, **5**, 19613-19618.
19. T. An, D. Deng, M. Lei, Q.-H. Wu, Z. Tian, M. Zheng and Q. Dong, *J. Mater. Chem. A*, 2016, **4**, 12858-12864.
20. K. Xie, Y. You, K. Yuan, W. Lu, K. Zhang, F. Xu, M. Ye, S. Ke, C. Shen, X. Zeng, X. Fan and B. Wei, *Adv. Mater.*, 2017, **29**, 1604724.
21. H. Xu and A. Manthiram, *Nano Energy*, 2017, **33**, 124-129.
22. Z. Sun, J. Zhang, L. Yin, G. Hu, R. Fang, H.-M. Cheng and F. Li, *Nat. commun.*, 2017, **8**, 14627.

23. Y. Pan, Y. Zhou, Q. Zhao, Y. Dou, S. Chou, F. Cheng, J. Chen, H. K. Liu, Lei Jiang and S. X. Dou, *Nano Energy*, 2017, **33**, 205-212.
24. W. Hua, Z. Yang, H. Nie, Z. Li, J. Yang, Z. Guo, C. Ruan, X. Chen and S. Huang, *ACS Nano*, 2017, **11**, 2209-2218.
25. J. Zhu, Y. Ge, D. Kim, Y. Lu, C. Chen, M. Jiang and X. Zhang, *Nano Energy*, 2016, **20**, 176-184.
26. Z. Zheng, H. Guo, F. Pei, X. Zhang, X. Chen, X. Fang, T. Wang and N. Zheng, *Adv. Funct. Mater.*, 2016, **26**, 8952-8959.
27. J. Zhang, Y. Shi, Y. Ding, W. Zhang and G. Yu, *Nano Lett.*, 2016, **16**, 7276-7281.
28. S. Yuan, J. L. Bao, L. Wang, Y. Xia, D. G. Truhlar and Y. Wang, *Adv. Energy Mater.*, 2016, **6**, 1501733.
29. M. Shaibani, A. Akbari, P. Sheath, C. D. Easton, P. C. Banerjee, K. Konstas, A. Fakhfouri, M. Barghamadi, M. M. Musameh, A. S. Best, T. Rüther, P. J. Mahon, M. R. Hill, A. F. Hollenkamp and M. Majumder, *ACS Nano*, 2016, **10**, 7768-7779.
30. K. Mi, Y. Jiang, J. Feng, Y. Qian and S. Xiong, *Adv. Funct. Mater.*, 2016, **26**, 1571-1579.
31. Y.-J. Li, J.-M. Fan, M.-S. Zheng and Q.-F. Dong, *Energy Environ. Sci.*, 2016, **9**, 1998-2004.
32. Z. Zhang, L. L. Kong, S. Liu, G.-R. Li and X.-P. Gao, *Adv. Energy Mater.*, 2017, **7**, 1602543.

33. H. Wei, E. F. Rodriguez, A. S. Best, A. F. Hollenkamp, D. Chen and R. A. Caruso, *Adv. Energy Mater.*, 2017, **7**, 1601616.

34. Y. Chen, S. Choi, D. Su, X. Gao and G. Wang, *Nano Energy*, 2018, **47**, 331-339.

35. H. Lin, L. Yang, X. Jiang, G. Li, T. Zhang, Q. Yao, G. Zheng and J. Y. Lee, *Energy Environ. Sci.*, 2017, **10**, 1476-1486.

36. A-Y. Kim, M. K. Kim, J. Y. Kim, Y. Wen, L, Gu, V.-D. Dao, H.-S, Choi, D, Byun and J. K. Lee, *Nano Res.*, 2017, **10**, 2083-2095.

37. Y. Hou, H. Mao and L. Xu, *Nano Res.*, 2017, **10**, 344-353.

38. Z. A. Ghazi, X. He, A. M. Khattak, N. A. Khan, B. Liang, A. Iqbal, J. Wang, H. Sin, L. Li and Z. Tang, *Adv. Mater.*, 2017, **29**, 1606817.

39. J. Zhang, H. Hu, Z. Li and X. W. Lou, *Angew. Chem. Int. Ed.*, 2016, **55**, 3982-3986.

40. Y. Tao, Y. Wei, Y. Liu, J. Wang, W. Qiao, L. Ling and D. Long, *Energy Environ. Sci.*, 2016, **9**, 3230-3239.

41. L. Sun, D. Wang, Y. Luo, K. Wang, W. Kong, Y. Wu, L. Zhang, K. Jiang, Q. Li, Y. Zhang, J. Wang and S. Fan, *ACS Nano*, 2016, **10**, 1300-1308.

42. D. Su, M. Cortie and G. Wang, *Adv. Energy Mater.*, 2017, **7**, 1602014.

43. S. Rehman, S. Guo and Y. Hou, *Adv. Mater.*, 2016, **28**, 3167-3172.

44. S. Rehman, X. Gu, K. Khan, N. Mahmood, W. Yang, X. Huang, S. Guo and Y. Hou, *Adv. Energy Mater.*, 2016, **6**, 1502518.

45. L. Ma, H. L. Zhuang, S. Wei, K. E. Hendrickson, M. S. Kim, G. Cohn, R. G. Hennig and L. A. Archer, *ACS Nano*, 2016, **10**, 1050-1059.

46. Z. Li, J. Zhang, B. Guan, D. Wang, L.-M. Liu and X. W. Lou, *Nat. Commun.*, 2016, **7**, 13065.

47. M. Li, Y. Zhang, X. Wang, W. Ahn, G. Jiang, K. Feng, G. Lui and Z. Chen, *Adv. Funct. Mater.*, 2016, **26**, 8408-8417.

48. Y.-L. Ding, P. Kopold, K. Hahn, P. A. Aken, J. Maier and Y. Yu, *Adv. Funct. Mater.*, 2016, **26**, 1112-1119.

49. Y. Dong, S. Zheng, J. Qin, X. Zhao, H. Shi, X. Wang, J. Chen and Z.-S. Wu, *ACS Nano*, 2018, **12**, 2381-2388.

50. W. Bao, D. Su, W, Zhang, X. Guo and G. Wang, *Adv. Funct. Mater.*, 2016, **26**, 8746-8756.