Supplementary Information

Boron-Nitride Based Dispersive Composite Coating on Nickel-Rich Layered Cathode for Enhanced Cycle Stability and Safety

Hsi Chen[1,3], Yan-Cheng Chen[1], Hao-Wen Liu[1], Shu-Jui Chang[1], Cheng-Hung Liao[1], Senthil-Kumar Parthasarathi[1], Satish Bolloju[1], Yu-Ting Weng[1], Jyh-Fu Lee[2], Jin-Ming Chen[2], Hwo-Shuenn Sheu[2], Chih-Wen Pao[2], and Nae-Lih Wu[1,3,*]

[1]*Department of Chemical Engineering, National Taiwan University, Taipei 10617, Taiwan.*

[2]*National Synchrotron Radiation Research Center, Hsinchu 30076, Taiwan.*

[3]*Advanced Research Center for Green Materials Science and Technology, National Taiwan University, Taipei, 106, Taiwan.*

[*]To whom correspondence should be addressed: *nlw001@ntu.edu.tw*

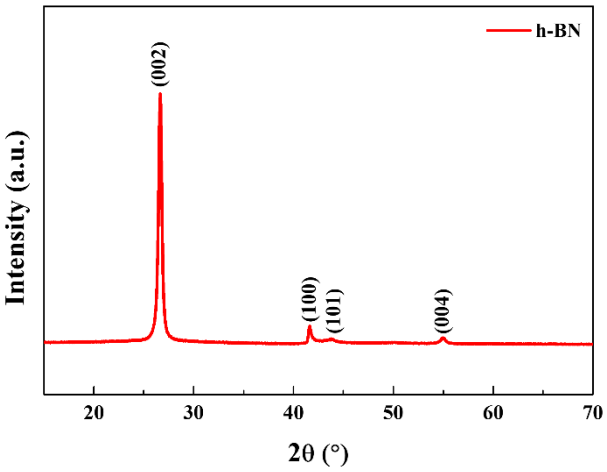

Figure S1. XRD pattern of h-BN.

Table S1. Rietveld refinement results of pristine NCM.

Sample	**NCM**				
Rwp (%)	1.39				
a (Å)	2.87157				
c (Å)	14.19595				
c/a	4.94362				
Volume (Å^3)	101.375				
Atom	**Site**	**x**	**y**	**z**	**Occupancy**
Mn	3a	0	0	0	0.05
Co					0.12
Ni					0.819
Li					0.0111(4)
Li	3b	0	0	1/2	0.989
Ni					0.0111(4)
O	6c	0	0	0.25700(4)	1

Table S2. Rietveld refinement results of NCM@PB.

Sample	**NCM@PB**				
Rwp (%)	1.49				
a (Å)	2.87199				
c (Å)	14.19788				
c/a	4.94357				
Volume (Å^3)	101.419				
Atom	**Site**	**x**	**y**	**z**	**Occupancy**
Mn	3a	0	0	0	0.05
Co					0.12
Ni					0.819
Li					0.0105(5)
Li	3b	0	0	1/2	0.989
Ni					0.0105(5)
O	6c	0	0	0.25757(4)	1

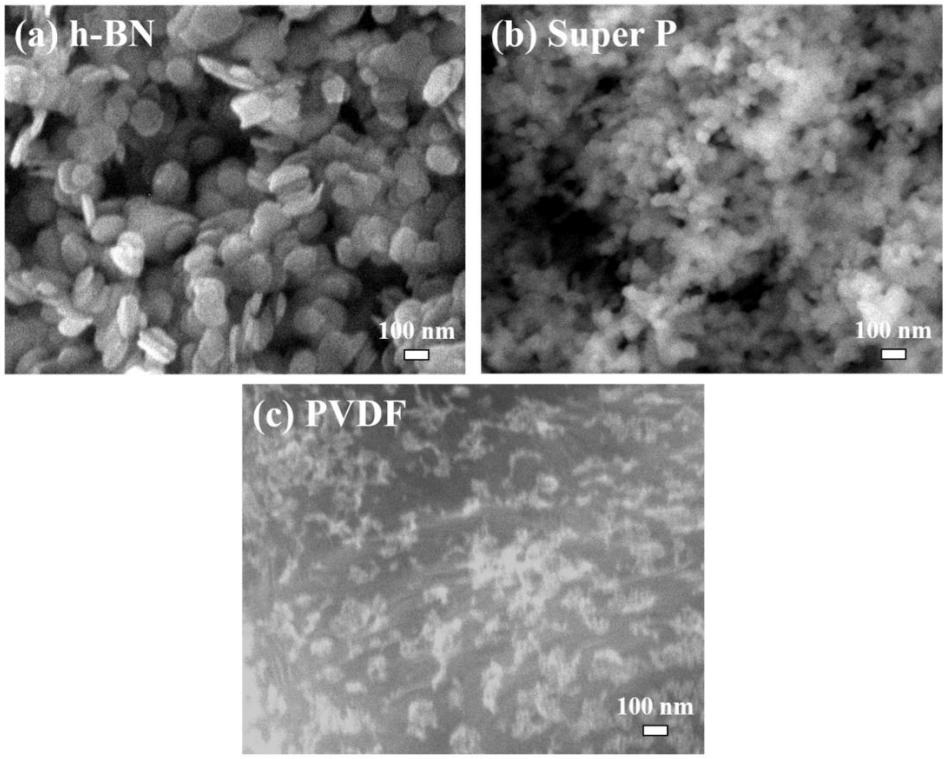

Figure S2. SEM images of (a) h-BN, (b) Super P and (c) calcined PVDF.

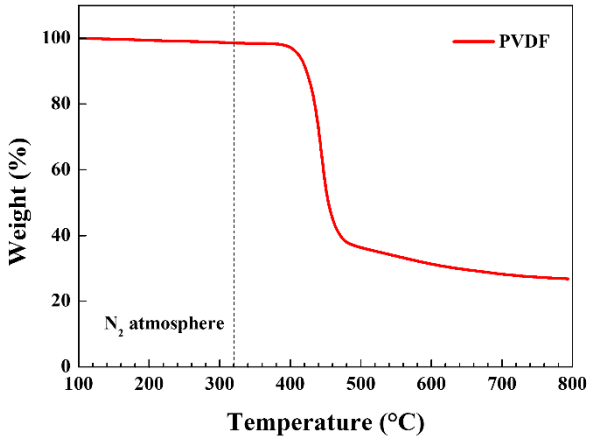

Figure S3. TGA curve of PVDF under N_2-atmosphere.

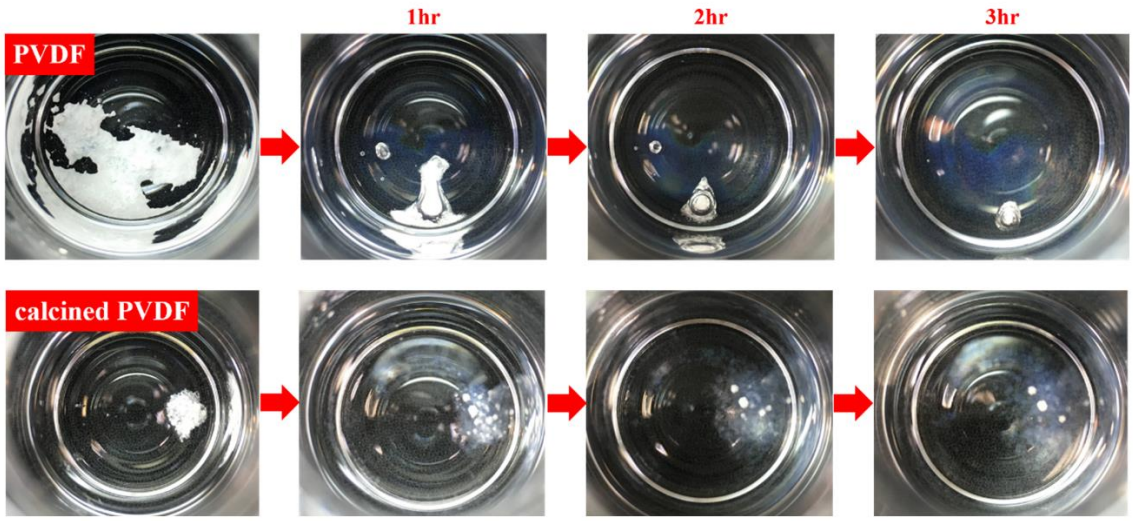

Figure S4. Solubility change of PVDF and 320°C calcined PVDF in NMP.

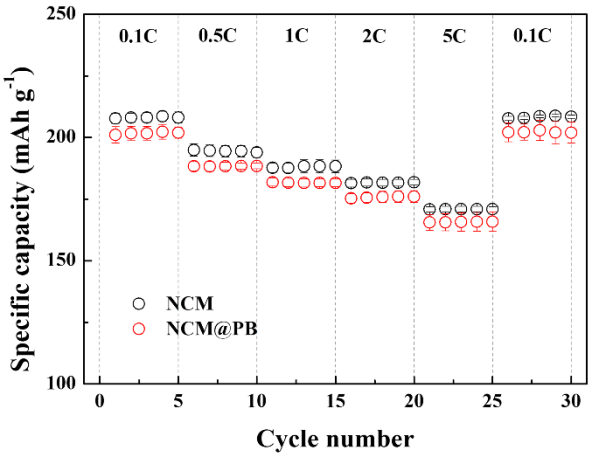

Figure S5. Rate capability of pristine NCM and NCM@PB (2.5-4.3V, error bars: standard deviation of three cells).

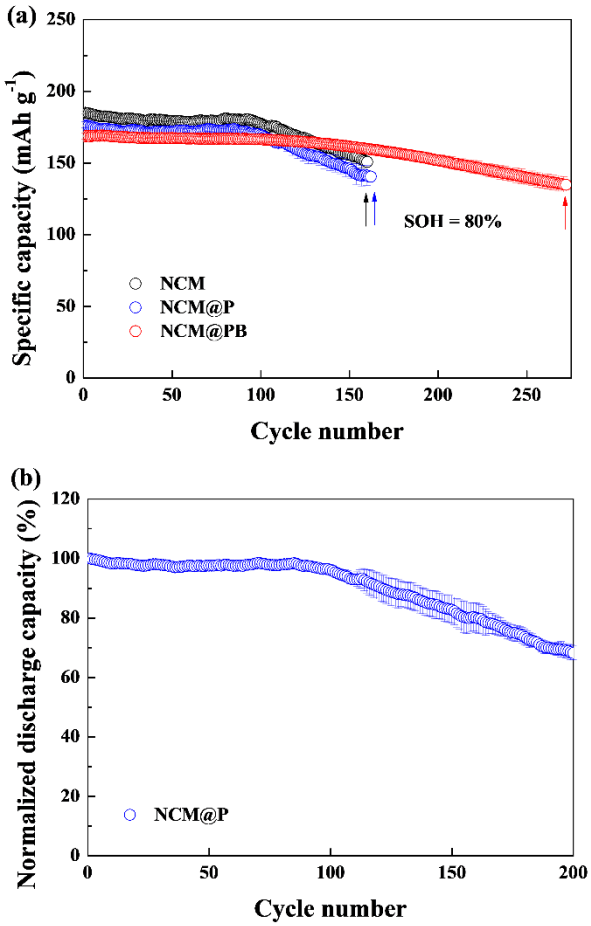

Figure S6. (a) Cycling performance of pristine NCM, NCM@P, NCM@PB at 1C-rate (2.5-4.3V; error bars: standard deviation of three cells) under room temperature; (b) Normalized cycling performance of NCM@P.

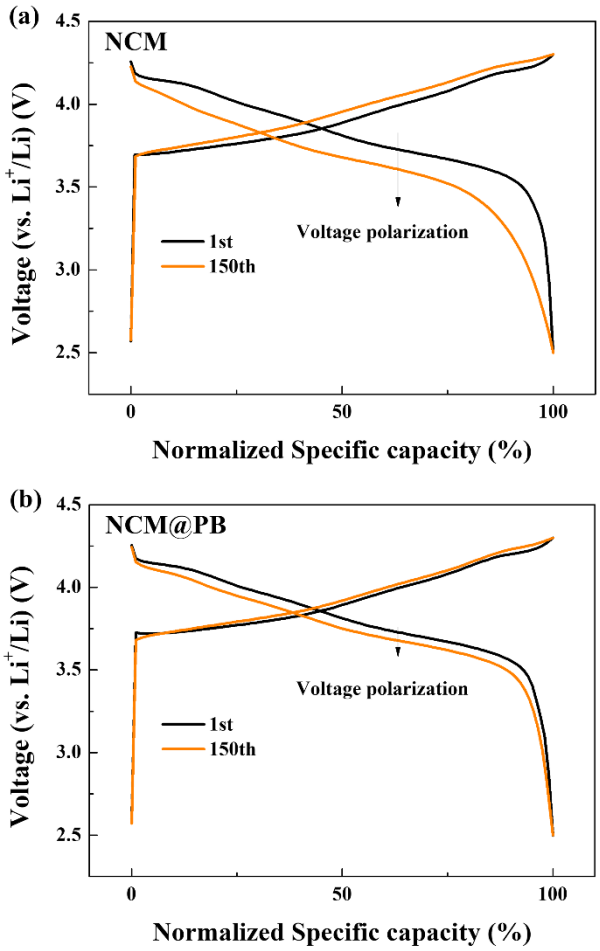

Figure S7. Normalized 1C-rate voltage profiles at different cycles of (a) pristine NCM and (b) NCM@PB.

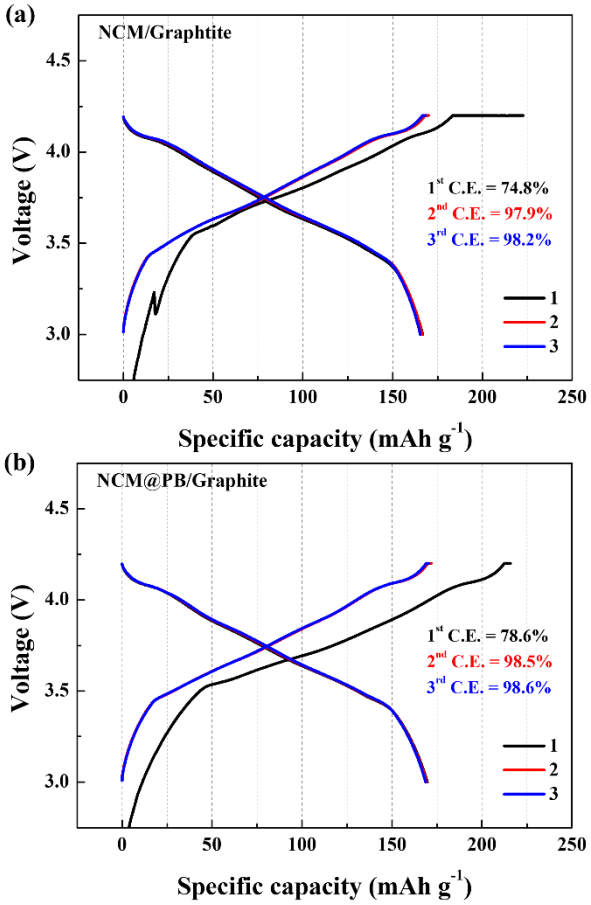

Figure S8. Formation cycles of (a) NCM/Graphite and (b) NCM@PB/Graphite full cells at 0.1C-rate.

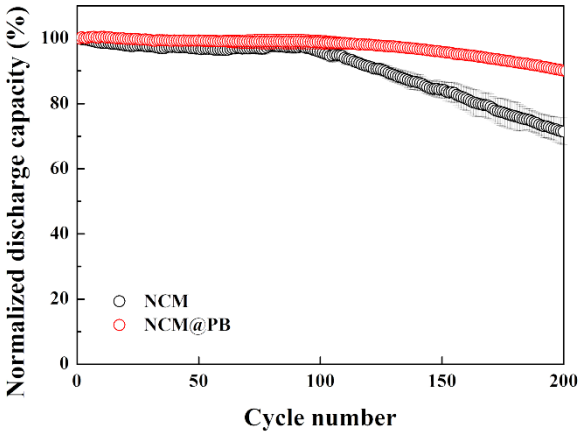

Figure S9. Normalized cycling performance of pristine NCM and NCM@PB at 1C-rate (2.5-4.3V; error bars: standard deviation of three cells).

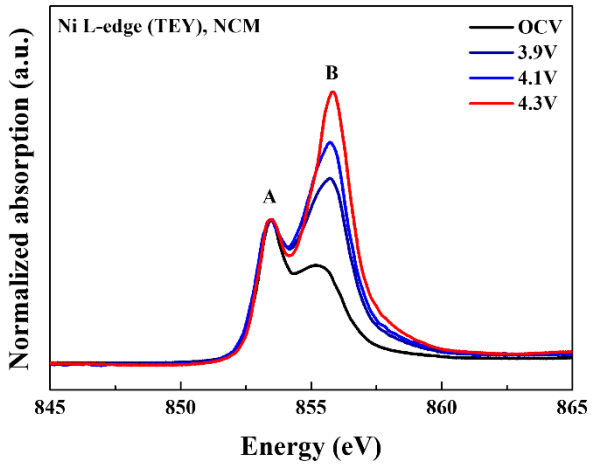

Figure S10. Ex situ Ni L_3-edge spectra of pristine NCM during charging of the 1st cycle.

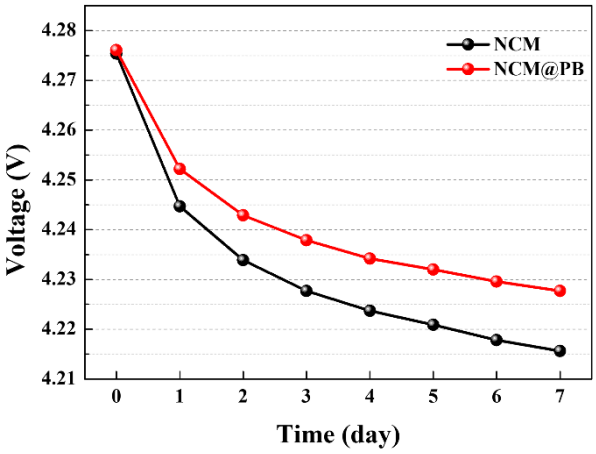

Figure S11. Self-discharge curves of pristine NCM and NCM@PB. Both cells were first charged to 4.3V and rest for 1 week. The voltage of both cells was recorded while resting. Note that the initial voltage is lower than 4.3V due to depolarization effect.

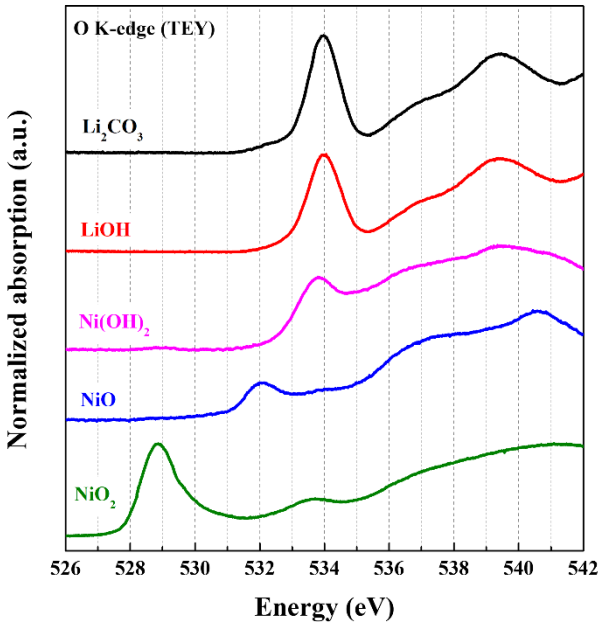

Figure S12. O K-edge spectra of Li_2CO_3, LiOH, $Ni(OH)_2$, NiO and NiO_2.

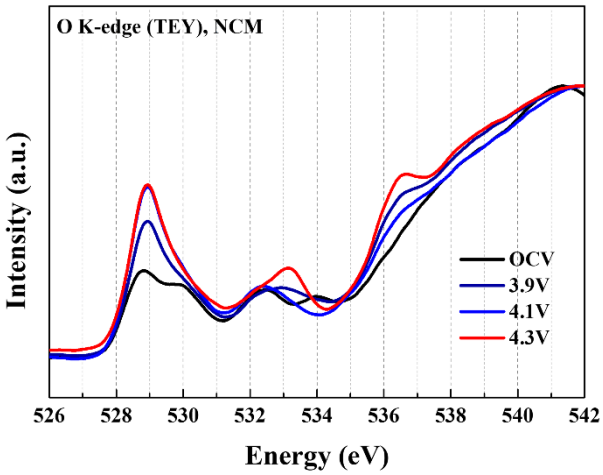

Figure S13. Ex situ O K-edge spectra of pristine NCM during charging of the 1st cycle.

Table S3. Summary of modification on Ni-rich cathodes

Surface modification material	Method	Cathode	Process temperature (time)	Voltage range (V v.s. Li^+/Li)	Cycle stability (25 °C)	Thermal stability	Full cell performance	Ref.
Zr^{4+}	Doping	$LiNi_{0.83}Co_{0.11}Mn_{0.06}O_2$	500 °C (6hr) → 830 °C (12hr)	3.0 – 4.3V	73.0%, 150th at 1C	N.A.	N.A.	1
Al^{3+}	Doping				74.7%, 150th at 1C			
Zr^{4+}/Al^{3+}	Doping				89.7%, 150th at 1C			
Mg^{2+}	Doping		480 °C (5hr) → 750 °C (15hr)	2.8 – 4.3V	84.5%, 200th at 2C	N.A.	N.A.	2
Li_3PO_4	Coating		480 °C (N.A.)		80.5%, 200th at 2C			
Mg^{2+}/Li_3PO_4	Doping +Coating		480 °C (5hr) → 750 °C (15hr) → 480 °C (N.A.)		90.0%, 200th at 2C			
Nb^{5+}	Doping		480 °C (5hr) → 750 °C (15hr)	2.8 – 4.3V	86.6%, 200th at 1C	N.A.	N.A.	3
Mo^{6+}/Li_2MoO_4	Doping +Coating		500 °C (12hr)	2.7 – 4.3V	90.22%, 100th at 1C	N.A.	N.A.	4
W^{6+}	Doping		80 °C (5hr) → 750 °C (15hr)	2.8 – 4.3V	69.9%, 500th at 2C	N.A.	N.A.	5

$Ti^{4+}/LaNiLiO_8$	Doping +Coating	$LiNi_{0.8}Co_{0.1}Mn_{0.1}O_2$	480 °C (5hr) → 830 °C (12hr)	2.7 – 4.3V	90.55%, 200th at 1C	15 °C-delayed decomp. temp. 43%-decreased heat release. 16%-decreased maximum heat flow.	N.A.	6
$LiAlO_2$	Coating		480 °C (5hr) → 750 °C (15hr)	2.8 – 4.3V	85.8%, 200th at 0.5C	11 °C-delayed decomp. temp. 47%-decreased heat release. 10%-decreased maximum heat flow.	N.A.	7
Li_3PO_4-$AlPO_4$-$Al(PO_3)_3$	Coating		600 °C (6hr)	3.0 – 4.3V	85.4%, 50th at 0.5C	6 °C-delayed decomp. temp. 22%-decreased heat release. 24%-decreased maximum heat flow.	71.8%, 100th at 0.5C	8
Li_2MnO_3	Coating		850 °C (5hr)	2.7 – 4.3V	80.4%, 500th at 1C	14 °C-delayed decomp. temp. 45%-decreased heat release. 27%-decreased maximum heat flow.	N.A.	9
$MgHPO_4$	Coating		500 °C (5hr) → 750 °C (15hr)	3.0 – 4.3V	86.3%, 100th at 0.5C	N.A.	N.A.	10
h-BN	**Coating**	$LiNi_{0.83}Co_{0.12}Mn_{0.05}O_2$	**320 °C (0.5hr)**	**2.5 – 4.3V**	**92.0%, 200th at 1C**	**40 °C-delayed decomp. temp. 44%-decreased heat release. 41%-decreased maximum heat flow.**	**80%-capacity mark: 360th cycle at 0.3C**	**This work**

References

1. Z. Zhu, Y. Liang, H. Hu, A. Gao, T. Meng, D. Shu, F. Yi and J. Ling, *Journal of Power Sources*, 2021, **498**, 229857.
2. W. Xiao, Y. Nie, C. Miao, J. Wang, Y. Tan and M. Wen, *Journal of Colloid and Interface Science*, 2022, **607**, 1071-1082.
3. J. Wang, Z. Yi, C. Liu, M. He, C. Miao, J. Li, G. Xu and W. Xiao, *Journal of Colloid and Interface Science*, 2023, **635**, 295-304.
4. T. Teng, L. Xiao, L. Shen, J. Ran, G. Xiang, Y. Zhu and H. Chen, *Applied Surface Science*, 2022, **601**, 154101.
5. J. Wang, C. Liu, Q. Wang, G. Xu, C. Miao, M. Xu, C. Wang and W. Xiao, *Journal of Colloid and Interface Science*, 2022, **628**, 338-349.
6. H. P. Yang, H. H. Wu, M. Y. Ge, L. J. Li, Y. F. Yuan, Q. Yao, J. Chen, L. F. Xia, J. M. Zheng, Z. Y. Chen, J. Duan, K. Kisslinger, X. C. Zeng, W. K. Lee, Q. B. Zhang and J. Lu, *Advanced Functional Materials*, 2019, **29**.
7. W. Tang, Z. Chen, F. Xiong, F. Chen, C. Huang, Q. Gao, T. Wang, Z. Yang and W. Zhang, *Journal of Power Sources*, 2019, **412**, 246-254.
8. Z. Feng, R. Rajagopalan, D. Sun, Y. G. Tang and H. Y. Wang, *Chemical Engineering Journal*, 2020, **382**.
9. X. Huang, W. Zhu, J. Yao, L. Bu, X. Li, K. Tian, H. Lu, C. Quan, S. Xu, K. Xu, Z. Jiang, X. Zhang, L. Gao and J. Zhao, *Journal of Materials Chemistry A*, 2020, **8**, 17429-17441.
10. D.-Y. Hwang, H.-S. Kim and S.-H. Lee, *Journal of Materials Chemistry A*, 2022, **10**, 16555-16569.