Supporting Information

Boron-doping-induced Defect Engineering Enables High-performance Graphene Cathode for Aluminum Batteries

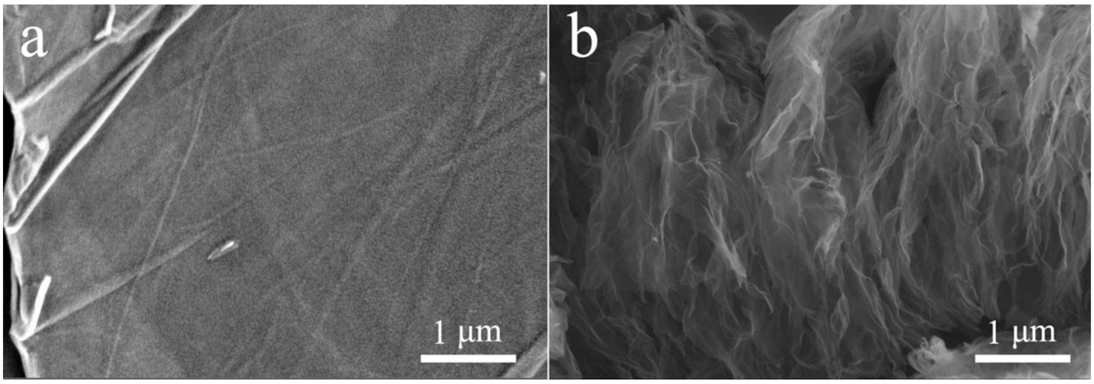

Fig. S1. The SEM images for (a) rGO and (b) BG samples.

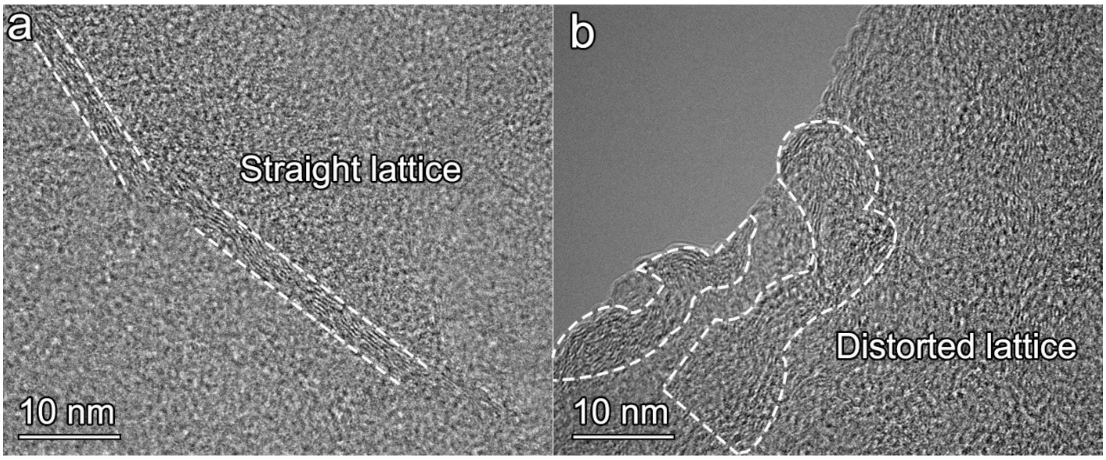

Fig. S2. The HRTEM images for (a) rGO and (b) BG samples.

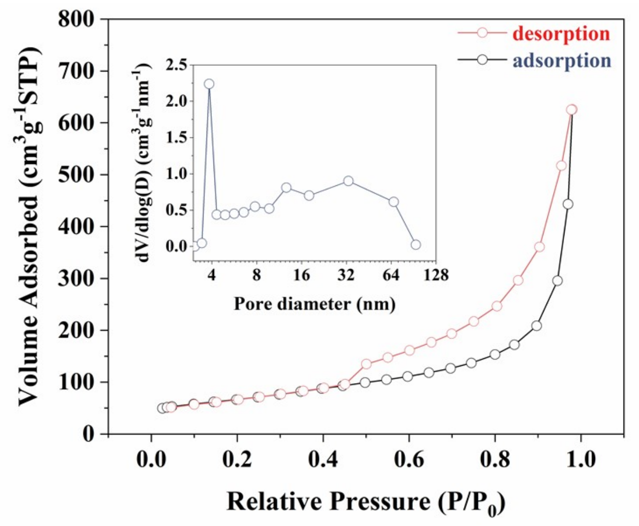

Fig. S3. The N_2 adsorption-desorption isotherms and the pore-size distributions (inset) for rGO sample.

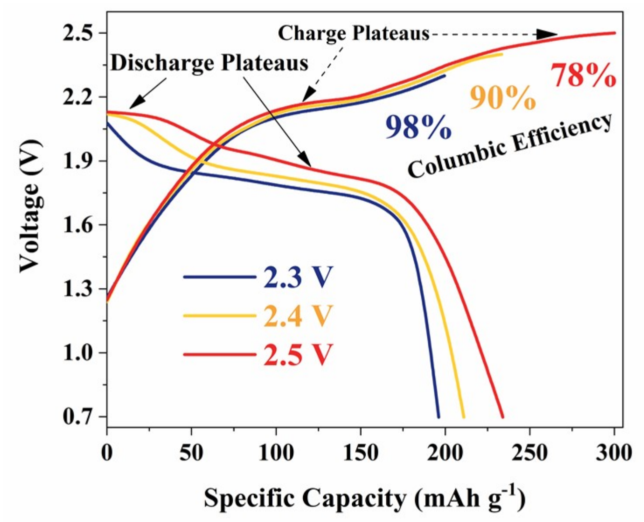

Fig. S4. The charge and discharge curves for the BG cathode upon cut-off voltages of 2.3 V, 2.4 V, and 2.5 V at 1 A g^{-1}.

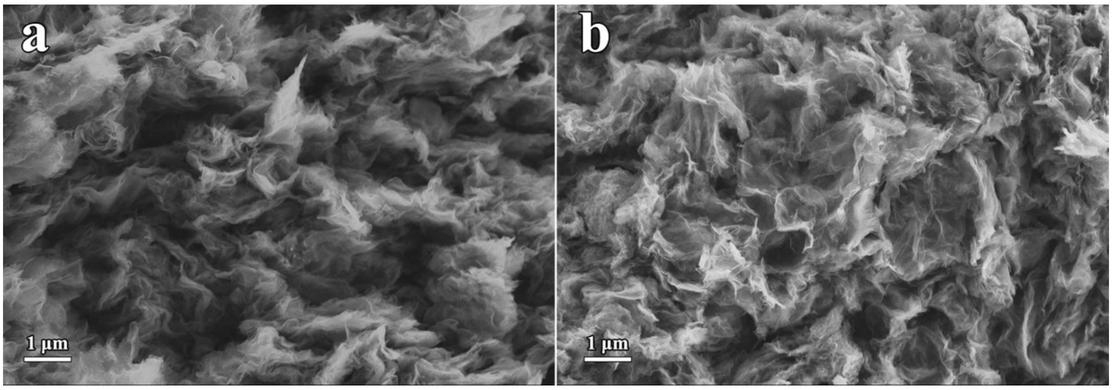

Fig. S5. The SEM images for the BG sample (a) before cycling and (b) after 100 cycles.

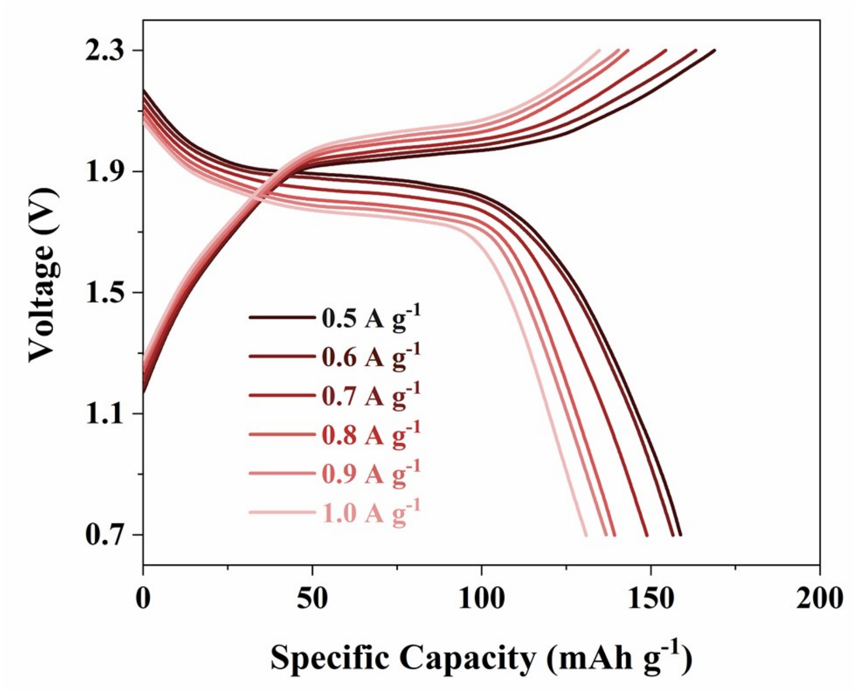

Fig. S6. The charge and discharge curves for the rGO cathode at different current densities.

Table S1. The comparison of the electrochemical performance between BG and other cathodes for RABs.

Cathode materials	Charge/discharge voltage (vs. Al)	Cycling performance	Ref.
BG	2.0 V/1.8 V	0.5 A g^{-1}/100 cycle/227 mAh g^{-1} 5 A g^{-1}/10000 cycle/135 mAh g^{-1}	This work
SnSe	2.0 V/1.6 V	0.3 A g^{-1}/100 cycle/107 mAh/g	1
VS_4	1.3 V/0.7 V	0.4 A g^{-1}/120 cycles/197 mAh g^{-1}	2
Expanded Graphite	2.1 V/2.0 V	2 A g^{-1}/300 cycles/111 mAh g^{-1}	3
$Ti_{0.95}\square_{0.05}O_{1.79}Cl_{0.08}(OH)_{0.13}$	1.2 V/1.0 V	3 A g^{-1}/110 cycles/64 mAh g^{-1}	4
Macrocyclic calix[4]quinone	1.0 V/ 0.8 V	0.2 A g^{-1}/50 cycles/269 mAh g^{-1}	5
$CoS_{1.097}$	1.5 V /0.7 V	0.1 A g^{-1}/500 cycles/80 mAh g^{-1}	6
Tetrachloro-1,4-benzoquinone	1.4 V /1.1 V	2 A g^{-1}/200 cycles/104 mAh g^{-1}	7
$K_2CuFe(CN)_6$	1.0 V/0.8 V	0.5 A g^{-1}/100 cycles/48 mAh g^{-1}	8
Surface-perforated graphene	2.0 V/1.8 V	2 A g^{-1}/200 cycles/197 mAh g^{-1}	9
N-doped C@ZnSe	2.1 V/1.8 V	1.5 A g^{-1}/500 cycles/61 mAh g^{-1}	10
Graphite flakes@carbon fiber	2.0 V/1.8 V	3 A g^{-1}/300 cycles/60 mAh g^{-1}	11
Graphite Nanoflakes	2.0 V/1.8 V	1 A g^{-1}/1000 cycles/100 mAh g^{-1}	12
Unzipped carbon nanotubes	2.0 V/1.8 V	5 A g^{-1}/5600 cycles/75 mAh g^{-1}	13
Graphene	2.3 V/2.2 V	3 A g^{-1}/1000 cycles/75 mAh g^{-1}	14
Carbon@graphene	1.9 V/1.8 V	4 A g^{-1}/10000 cycles/98 mAh g^{-1}	15
Graphitic foam	2.1 V/1.9 V	4 A g^{-1}/7500 cycles/70 mAh g^{-1}	16
SnS_2	1.6 V/0.7 V	0.2 A g^{-1}/100 cycles/70 mAh g^{-1}	17
C@N-C@N,P-C	1.3 V/0.5 V	5 A g^{-1}/2500 cycles/98 mAh g^{-1}	18
$CoSe_2$/C-ND@rGO	1.8 V/0.9 V	1 A g^{-1}/500 cycles/143 mAh g^{-1}	19
$Co_3(PO_4)_2$@C	1.2 V/1.3 V	2 A g^{-1}/500 cycles/151 mAh g^{-1}	20
Co_3S_4	0.9 V/0.7 V	0.05 A g^{-1}/150 cycles/90 mAh g^{-1}	21
CoSe	1.9 V/ 1.9 V	5 A g^{-1}/100 cycles/63 mAh g^{-1}	22
CuO	0.8 V/0.6 V	0.2 A g^{-1}/100 cycles/113 mAh g^{-1}	23
Ni_3S_2@Graphene	1.5 V/1.0 V	0.2 A g^{-1}/300 cycle/50 mAh g^{-1}	24
CuS@C	1.9 V/1.0 V	0.02 A g^{-1}/100 cycle/90 mAh g^{-1}	25
NiCo-sulfide	2.0 V/1.6 V	1 A g^{-1}/100 cycle/83 mAh g^{-1}	26
Cu_3P/C	1.0 V/0.8 V	0.05 A g^{-1}/50 cycle/147 mAh g^{-1}	27
V_2CT_x MXene	1.4 V/1.0 V	0.1 A g^{-1}/100 cycle/90 mAh g^{-1}	28
Co-P/CC	1.0 V/0.8 V	0.2 A g^{-1}/400 cycle/85 mAh g^{-1}	29
VS_4/rGO	1.6 V/1.0 V	0.2 A g^{-1}/100 cycle/70 mAh g^{-1}	30

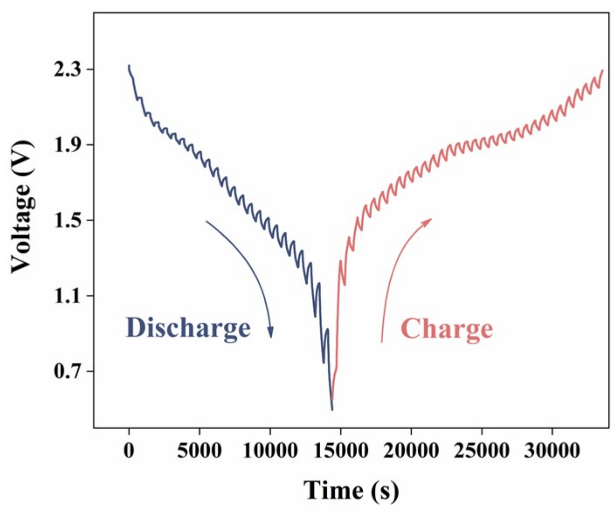

Fig. S7. The GITT curve for the rGO cathode.

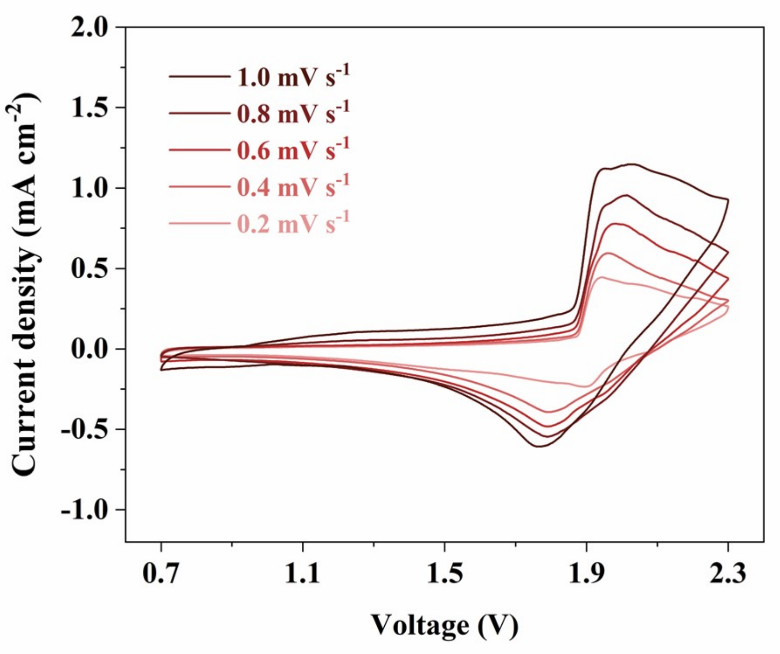

Fig. S8. The CV curves for the rGO cathode at different scan rates.

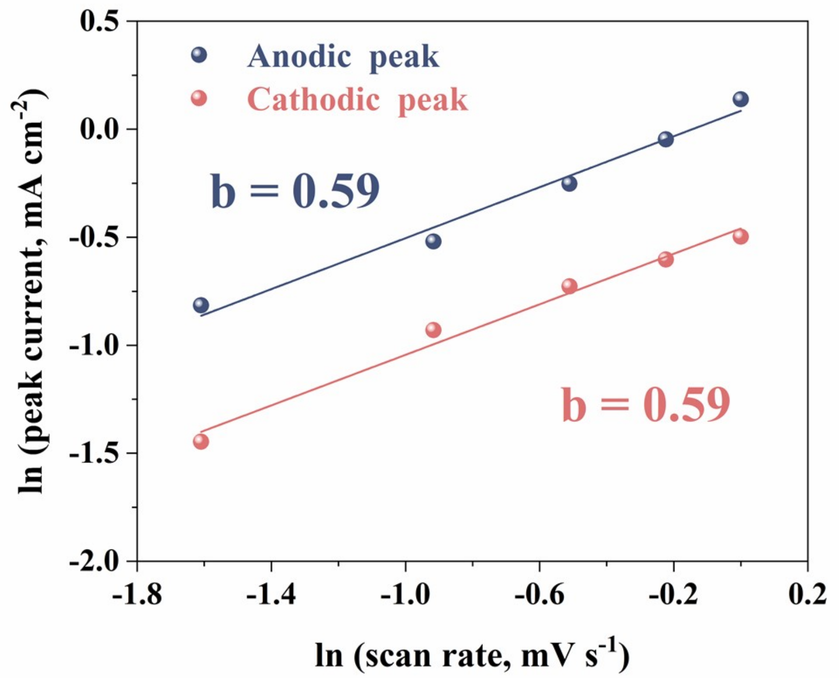

Fig. S9. The plot of ln(*i*) versus ln(*v*) for the rGO electrode.

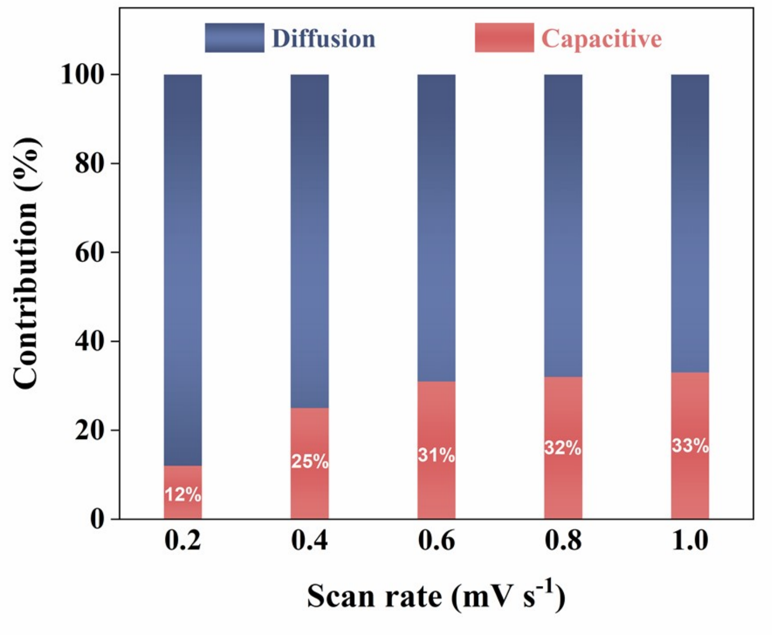

Fig. S10. The percentage of capacitive contribution for the rGO electrode upon different scan rates.

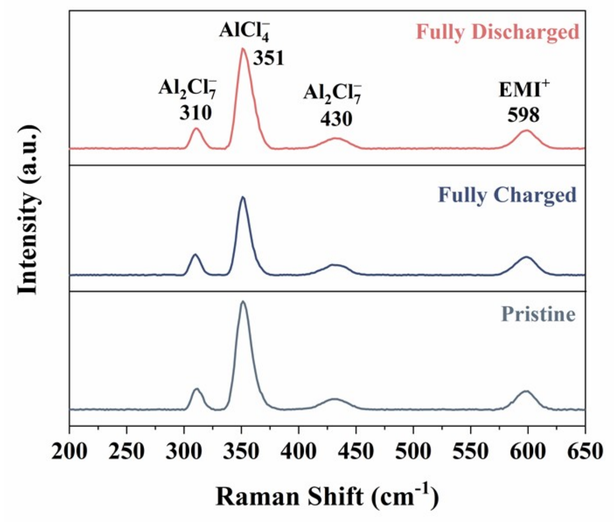

Fig. S11. The ex-situ Raman spectra for $AlCl_3$/[EMIm]Cl ionic liquid on the BG cathode surface.

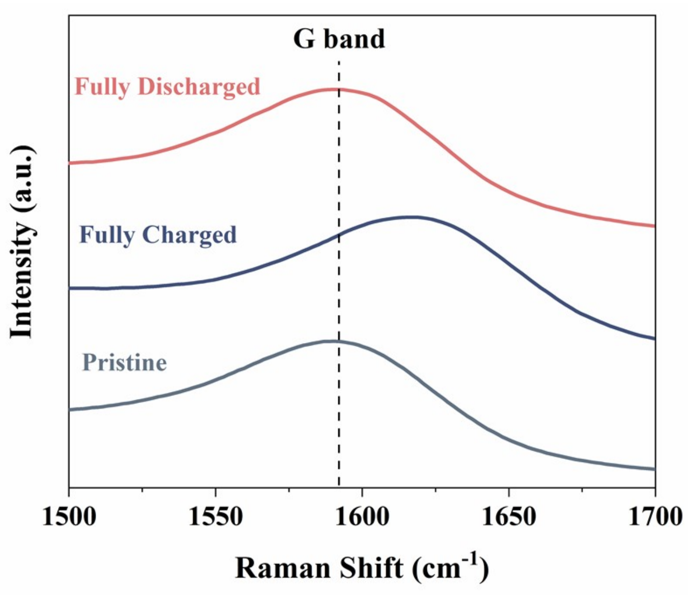

Fig. S12. The Raman spectra for the rGO cathode upon diverse states.

References

1. Y. Zhang, B. Zhang, J. Li, J. Liu, X. Huo and F. Kang, SnSe nano-particles as advanced positive electrode materials for rechargeable aluminum-ion batteries, Chemical Engineering Journal, 2021, **403**, 126377.
2. L. Xing, K. A. Owusu, X. Liu, J. Meng, K. Wang, Q. An and L. Mai, Insights into the storage mechanism of VS4 nanowire clusters in aluminum-ion battery, Nano Energy, 2021, **79**, 105384.
3. S. Guo, H. Yang, M. Liu, X. Feng, Y. Gao, Y. Bai and C. Wu, Al-Storage Behaviors of Expanded Graphite as High-Rate and Long-Life Cathode Materials for Rechargeable Aluminum Batteries, ACS Applied Materials & Interfaces, 2021, **13**, 22549-22558.
4. X. Wu, N. Qin, F. Wang, Z. Li, J. Qin, G. Huang, D. Wang, P. Liu, Q. Yao, Z. Lu and J. Deng, Reversible aluminum ion storage mechanism in Ti-deficient rutile titanium dioxide anode for aqueous aluminum-ion batteries, Energy Storage Materials, 2021, **37**, 619-627.
5. Y. Li, L. Liu, Y. Lu, R. Shi, Y. Ma, Z. Yan, K. Zhang and J. Chen, High-Energy-Density Quinone-Based Electrodes with [Al(OTF)]2+ Storage Mechanism for Rechargeable Aqueous Aluminum Batteries, Advanced Functional Materials, 2021, **31**, 2102063.
6. R. Zhuang, G. Miao, Z. Huang, Q. Zhang, J.-C. Wu and J. Yang, Non-stoichiometric CoS1.097 nanoparticles prepared from CoAl-layered double hydroxide and MOF template as cathode materials for aluminum-ion batteries, Journal of Energy Chemistry, 2021, **54**, 639-643.
7. J. He, X. Shi, C. Wang, H. Zhang, X. Liu, Z. Yang and X. Lu, A quinone electrode with reversible phase conversion for long-life rechargeable aqueous aluminum–metal batteries, Chemical Communications, 2021, DOI: 10.1039/D1CC02024B.
8. L. Yan, X. Zeng, S. Zhao, W. Jiang, Z. Li, X. Gao, T. Liu, Z. Ji, T. Ma, M. Ling and C. Liang, 9,10-Anthraquinone/K2CuFe(CN)6: A Highly Compatible Aqueous Aluminum-Ion Full-Battery Configuration, ACS Applied Materials & Interfaces, 2021, **13**, 8353-8360.
9. Y. Kong, C. Tang, X. Huang, A. K. Nanjundan, J. Zou, A. Du and C. Yu, Thermal Reductive Perforation of Graphene Cathode for High-Performance Aluminum-Ion Batteries, Advanced Functional Materials, 2021, **31**, 2010569.
10. J. Li, W. Liu, Z. Yu, J. Deng, S. Zhong, Q. Xiao, F. chen and D. Yan, N-doped C@ZnSe as a low cost positive electrode for aluminum-ion batteries: Better electrochemical performance with high voltage platform of ~1.8 V and new reaction mechanism, Electrochimica Acta, 2021, **370**, 137790.
11. C. Liu, Z. Liu, Q. Li, H. Niu, C. Wang, Z. Wang and B. Gao, Binder-free ultrasonicated graphite flakes@carbon fiber cloth cathode for rechargeable aluminum-ion battery, Journal of Power Sources, 2019, **438**, 226950.
12. H. Hu, T. Cai, P. Bai, J. Xu, S. Ge, H. Hu, M. Wu, Q. Xue, Z. Yan, X. Gao and W. Xing, Small graphite nanoflakes as an advanced cathode material for aluminum ion batteries, Chemical Communications, 2020, **56**, 1593-1596.
13. E. Zhang, J. Wang, B. Wang, X. Yu, H. Yang and B. Lu, Unzipped carbon nanotubes for aluminum battery, Energy Storage Materials, 2019, **23**, 72-78.
14. A. S. Childress, P. Parajuli, J. Zhu, R. Podila and A. M. Rao, A Raman spectroscopic study of graphene cathodes in high-performance aluminum ion batteries, Nano Energy, 2017, **39**, 69-76.
15. Z. Liu, J. Wang, X. Jia, W. Li, Q. Zhang, L. Fan, H. Ding, H. Yang, X. Yu, X. Li and B. Lu, Graphene Armored with a Crystal Carbon Shell for Ultrahigh-Performance Potassium Ion Batteries and Aluminum Batteries, ACS Nano, 2019, **13**, 10631-10642.

16. M.-C. Lin, M. Gong, B. Lu, Y. Wu, D.-Y. Wang, M. Guan, M. Angell, C. Chen, J. Yang, B.-J. Hwang and H. Dai, An ultrafast rechargeable aluminium-ion battery, Nature, 2015, **520**, 324.
17. Y. Hu, B. Luo, D. Ye, X. Zhu, M. Lyu and L. Wang, An Innovative Freeze-Dried Reduced Graphene Oxide Supported SnS2 Cathode Active Material for Aluminum-Ion Batteries, Advanced Materials, 2017, **29**, 1606132.
18. C. Li, S. Dong, R. Tang, X. Ge, Z. Zhang, C. Wang, Y. Lu and L. Yin, Heteroatomic interface engineering in MOF-derived carbon heterostructures with built-in electric-field effects for high performance Al-ion batteries, Energy & Environmental Science, 2018, **11**, 3201-3211.
19. T. Cai, L. Zhao, H. Hu, T. Li, X. Li, S. Guo, Y. Li, Q. Xue, W. Xing, Z. Yan and L. Wang, Stable CoSe2/carbon nanodice@reduced graphene oxide composites for high-performance rechargeable aluminum-ion batteries, Energy & Environmental Science, 2018, **11**, 2341-2347.
20. C. Li, S. Dong, P. Wang, C. Wang and L. Yin, Metal–Organic Frameworks-Derived Tunnel Structured Co3(PO4)2@C as Cathode for New Generation High-Performance Al-Ion Batteries, Advanced Energy Materials, 2019, **9**, 1902352.
21. H. Li, H. Yang, Z. Sun, Y. Shi, H.-M. Cheng and F. Li, A highly reversible Co3S4 microsphere cathode material for aluminum-ion batteries, Nano Energy, 2019, **56**, 100-108.
22. W. Xing, D. Du, T. Cai, X. Li, J. Zhou, Y. Chai, Q. Xue and Z. Yan, Carbon-encapsulated CoSe nanoparticles derived from metal-organic frameworks as advanced cathode material for Al-ion battery, Journal of Power Sources, 2018, **401**, 6-12.
23. X. Zhang, G. Zhang, S. Wang, S. Li and S. Jiao, Porous CuO microsphere architectures as high-performance cathode materials for aluminum-ion batteries, Journal of Materials Chemistry A, 2018, **6**, 3084-3090.
24. S. Wang, Z. Yu, J. Tu, J. Wang, D. Tian, Y. Liu and S. Jiao, A Novel Aluminum-Ion Battery: Al/AlCl3-[EMIm]Cl/Ni3S2@Graphene, Advanced Energy Materials, 2016, **6**, 1600137.
25. S. Wang, S. Jiao, J. Wang, H.-S. Chen, D. Tian, H. Lei and D.-N. Fang, High-Performance Aluminum-Ion Battery with CuS@C Microsphere Composite Cathode, ACS Nano, 2017, **11**, 469-477.
26. W. Xing, X. Li, T. Cai, Y. Zhang, P. Bai, J. Xu, H. Hu, M. Wu, Q. Xue, Y. Zhao, J. Zhou, S. Zhuo, X. Gao and Z. Yan, Layered double hydroxides derived NiCo-sulfide as a cathode material for aluminum ion batteries, Electrochimica Acta, 2020, **344**, 136174.
27. G. Li, J. Tu, M. Wang and S. Jiao, Cu3P as a novel cathode material for rechargeable aluminum-ion batteries, Journal of Materials Chemistry A, 2019, **7**, 8368-8375.
28. A. VahidMohammadi, A. Hadjikhani, S. Shahbazmohamadi and M. Beidaghi, Two-Dimensional Vanadium Carbide (MXene) as a High-Capacity Cathode Material for Rechargeable Aluminum Batteries, ACS Nano, 2017, **11**, 11135-11144.
29. S. Lu, M. Wang, F. Guo, J. Tu, A. Lv, Y. Chen and S. Jiao, Self-supporting and high-loading hierarchically porous Co-P cathode for advanced Al-ion battery, Chemical Engineering Journal, 2020, **389**, 124370.
30. X. F. Zhang, S. Wang, J. G. Tu, G. H. Zhang, S. J. Li, D. H. Tian and S. Q. Jiao, Flower-like Vanadium Suflide/Reduced Graphene Oxide Composite: An Energy Storage Material for Aluminum-Ion Batteries, ChemSusChem, 2018, **11**, 709-715.