

Supporting Information

**Metal-Organic Frameworks Derived Nitrogen-doped
Carbon-Confined CoSe₂ Anchored on Multiwall Carbon
Nanotube Networks as Anode for High-rate Sodium-ion
Batteries**

*Lei Chen¹, Xuefan Wang¹, Yijiao Ding¹, Yuke Li^{1,2}, Shi-Bin Ren^{*1}, Mao Shen¹, Yu-
Xiang Chen¹, Wei Li¹, and De-Man Han^{**1}*

¹ School of Pharmaceutical Chemical and Materials Engineering, Taizhou University,
Taizhou, 318000, P. R. China

² Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, 310018, P. R.
China

*Corresponding author.

E-mail address: renshibin@tzc.edu.cn; hdm@tzc.edu.cn.

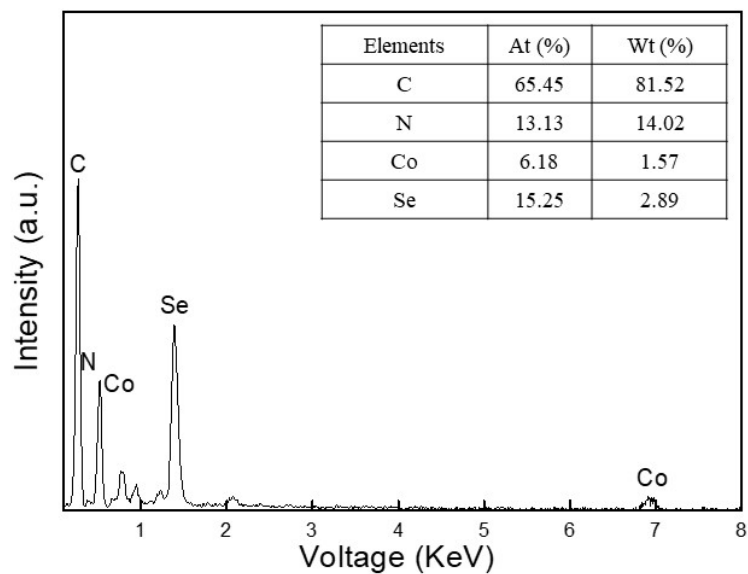


Figure S1. EDS spectrum of CoSe₂@NC/MWCNTs (the inset table is atomic and weight ratios of Co, Se, N and C in CoSe₂@NC/MWCNTs composite).

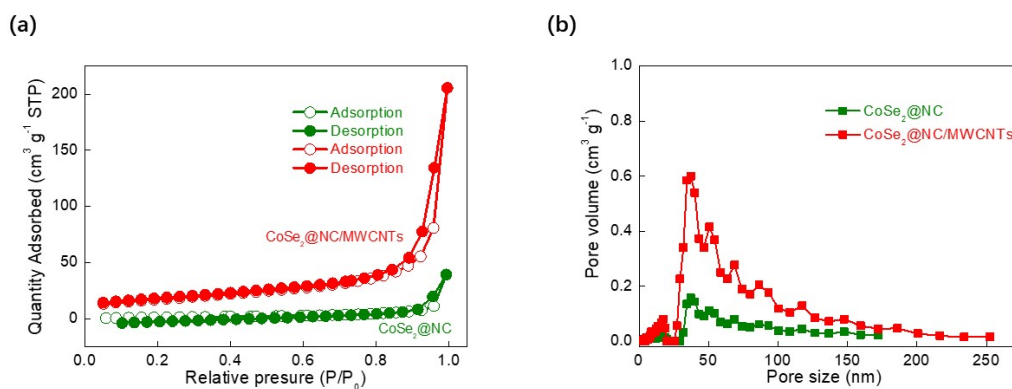


Figure S2. The nitrogen adsorption-desorption isotherms (a) and pore size distributions (b) of CoSe₂@NC and CoSe₂@NC/MWCNTs composites.

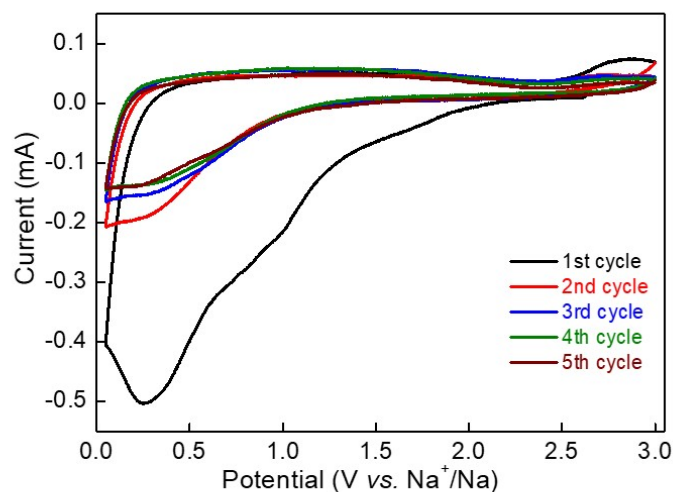


Figure S3. CV curves of the $\text{CoSe}_2@\text{NC}$ electrode at scan rate of 0.2 mV s^{-1} for the initial fifth cycles.

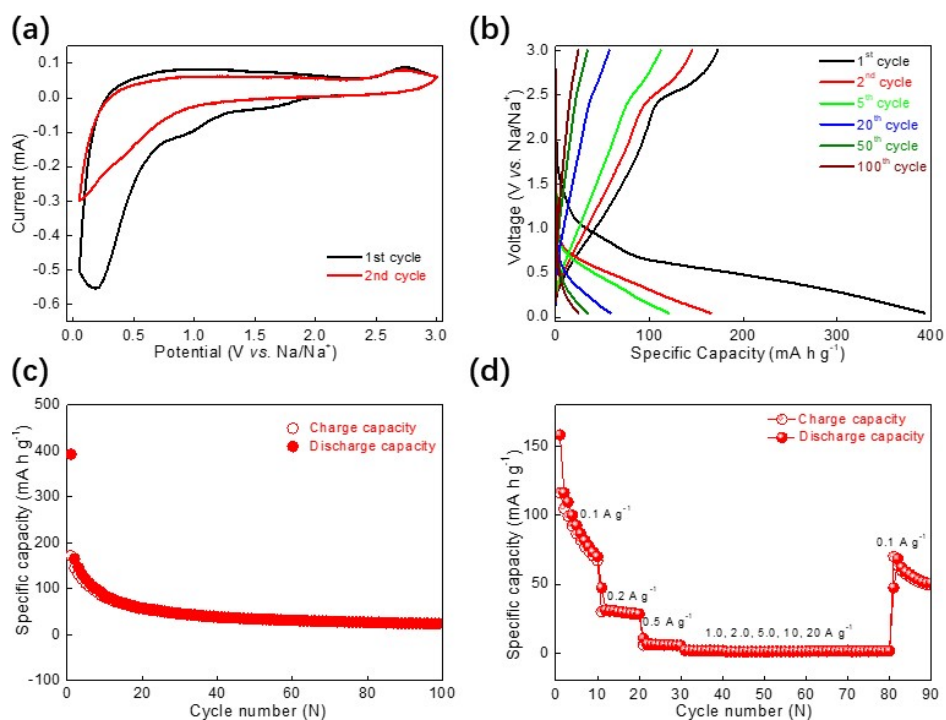


Figure S4. Electrochemical performance of $\text{Co}@\text{NC}$ electrodes in the voltage window $0.05\text{-}3.0 \text{ V}$ (V vs. Na/Na^+): (a) CV curves at scan rate of 0.1 mV s^{-1} for the initial three cycles; (b) Galvanostatic discharge/charge profiles of 1^{st} , 2^{nd} , 5^{th} , 20^{th} , 50^{th} and 100^{th} cycles at a current density of 0.1 A g^{-1} ; (c) Cycling performance at 0.1 A g^{-1} over 100 cycles; (d) Rate capability at different current densities of $0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10$ and 20 A g^{-1} .

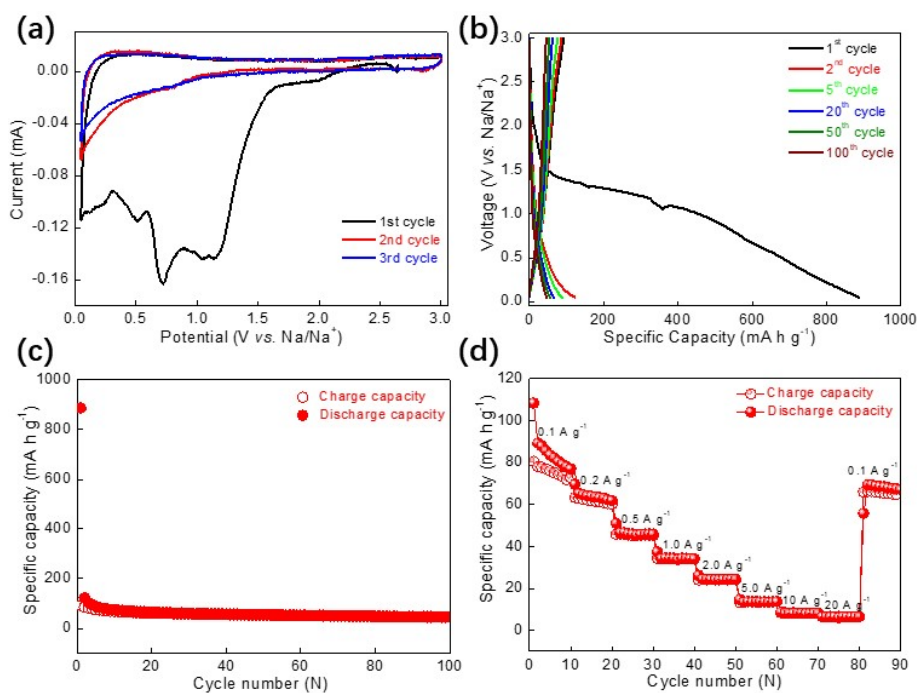


Figure S5. Electrochemical performance of MWCNTs electrodes in the voltage window 0.05-3.0

V (V vs. Na/Na⁺): (a) CV curves at scan rate of 0.1 mV s⁻¹ for the initial three cycles; (b) Galvanostatic discharge/charge profiles of 1st, 2nd, 5th, 20th, 50th and 100th cycles at a current density of 0.1 A g⁻¹; (c) Cycling performance at 0.1 A g⁻¹ over 100 cycles; (d) Rate capability at different current densities of 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10 and 20 A g⁻¹.

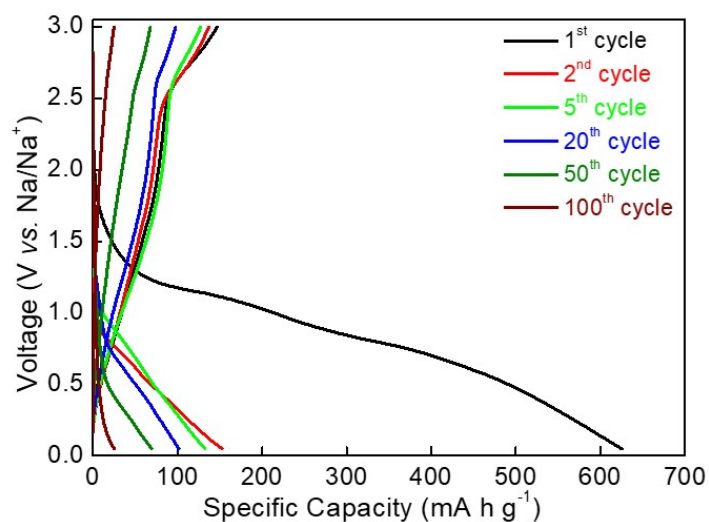


Figure S6. Galvanostatic discharge/charge profiles of the 1st, 2nd, 5th, 20th, 50th and 100th cycles for CoSe₂@NC electrode at a current density of 0.2 A g⁻¹.

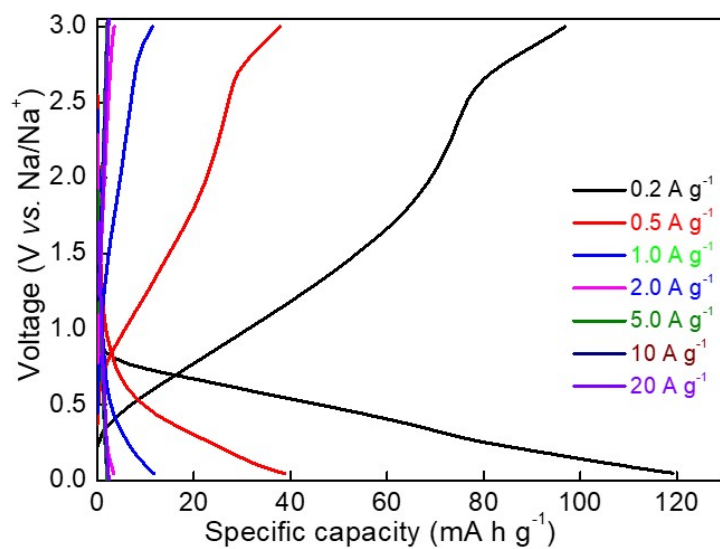


Figure S7. The charge/discharge profiles of CoSe₂@NC at the various current densities.

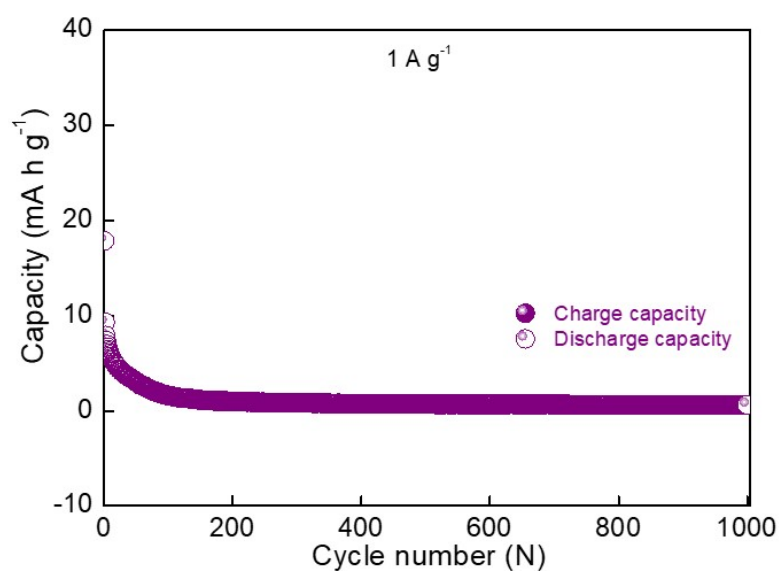


Figure S8. The long-cycling performance of CoSe₂@NC electrode at 1.0A g⁻¹ over 1000 cycles.

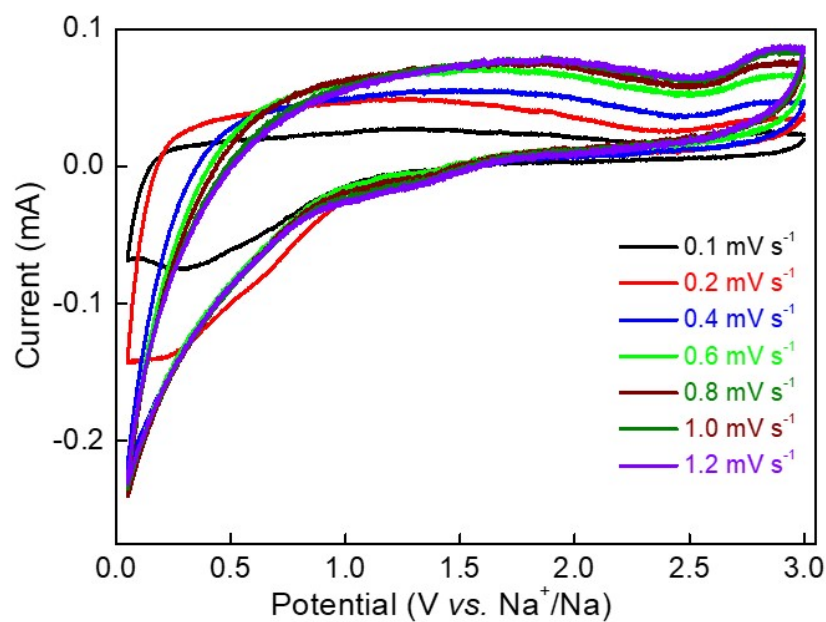


Figure S9. CV curves of CoSe₂@NC electrode at various scan rates from 0.1 to 1.2 mV s⁻¹.

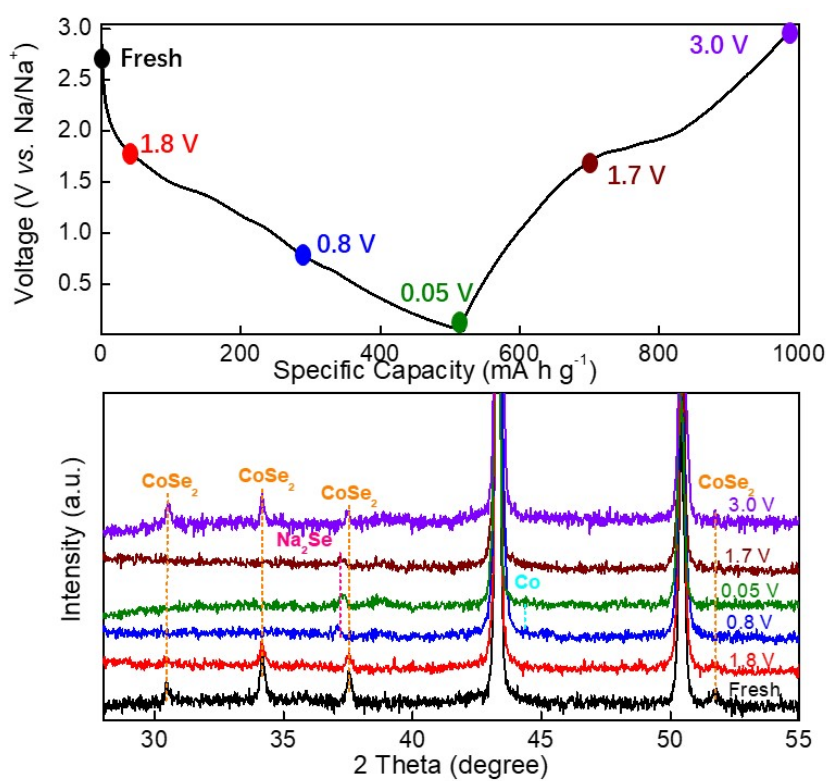


Figure S10. Ex-situ XRD analysis of the CoSe₂@NC/MWCNTs electrode at different charge-discharge states.

Table S1. Elemental composition of CoSe₂@NC/MWCNTs determined from XPS result.

Element	Peak (eV)	Height	FWHM (eV)	Atomic (%)
C1s	284.8	58711.08	0.82	94.36
Co2p	781.23	3084.39	3.09	0.54
Se3d	55.99	445.16	1.33	1.04
N1s	399.09	2177.8	1.2	4.04

Table S2. Comparison of the electrochemical performance of CoSe₂@NC/MWCNTs composite with previously reported CoSe₂-based anode for SIBs.

Samples	Initial Capacity (mA h g ⁻¹)	Long-cycling performance	Rate property (mA h g ⁻¹)	Ref.
CoSe ₂ @N-CA	496 (0.2 A g ⁻¹)	373 at 3.0 A g ⁻¹ (2000 cycles)	337 (10 A g ⁻¹)	S1
CoSe ₂ @NC/MX	462 (0.5 A g ⁻¹)	317 at 0.5 A g ⁻¹ (200 cycles)	343 (7 A g ⁻¹)	S2
N-CoSe ₂ yss	602.3 (0.2 A g ⁻¹)	500 at 10 A g ⁻¹ (1000 cycles)	431 (50 A g ⁻¹)	S3
CoSe ₂ -CNS	535 (0.2 A g ⁻¹)	250 at 10 A g ⁻¹ (2000 cycles)	352 (10 A g ⁻¹)	S4
CoSe ₂ @C∩NC	389 (0.1 A g ⁻¹)	234 at 5 A g ⁻¹ (2000 cycles)	146 (25 A g ⁻¹)	S5
CoSe ₂ @NC	356 (0.2 A g ⁻¹)	384.3 at 2 A g ⁻¹ (1800 cycles)	276.4 (5 A g ⁻¹)	S6
CoSe ₂ /N-CNF	371.8 (0.2 A g ⁻¹)	308 at 2 A g ⁻¹ (1000 cycles)	295.1 (2 A g ⁻¹)	S7
CoSe ₂ /NC	541 (0.1 A g ⁻¹)	390.5 at 5 A g ⁻¹ (4000 cycles)	376.5 (10 A g ⁻¹)	S8
N-CNT/rGO/CoSe ₂ NF	531 (0.5 A g ⁻¹)	264 at 10 A g ⁻¹ (10000 cycles)	151 (20 A g ⁻¹)	S9
CoSe ₂ @NC-NR/CNT	699 (0.2 A g ⁻¹)	555 at 0.2 A g ⁻¹ (100 cycles)	517 (5 A g ⁻¹)	S10
CNT-CoSe ₂ @NC	461.7 (0.2 A g ⁻¹)	404 at 0.2 A g ⁻¹ (120 cycles)	363 (5 A g ⁻¹)	S11
CNT/CoSe ₂ /C	531 (0.1 A g ⁻¹)	396 at 0.5 A g ⁻¹ (300 cycles)	223.6 (2.4 A g ⁻¹)	S12
CoSe ₂ @C/CNTs	470 (0.2 A g ⁻¹)	390 at 1 A g ⁻¹	373 (10 A g ⁻¹)	S13

		(1000 cycles)		
CoSe₂@NC/MW CNTs	479.6 (0.2 A g⁻¹)	131.5 at 5 A g⁻¹ (5000 cycles)	227.3 mA h g⁻¹ at 20 A g⁻¹	This work

Table S3. The calculated values of the equivalent circuit components for both samples.

Samples	R _e (Ω)	R _{SEI} (Ω)	CPE ₁ (F)	R _{ct} (Ω)	CPE ₂ (F)
CoSe ₂ @NC	9.59	418.9	9.74×10 ⁻⁶	27.6	1.55×10 ⁻⁵
CoSe ₂ @NC/MWCNTs	21.13	19.05	3.29×10 ⁻³	39.8	2.59×10 ⁻⁵

Table S4. Values of the equivalent circuit components for CoSe₂@NC/MWCNTs at different states.

Status	R _e (Ω)	R _s (Ω)	CPE ₁ (F)	R _{ct} (Ω)	CPE ₂ (F)
OCV	13.23	291.9	5.04×10 ⁻⁶	7.9	2.44×10 ⁻⁵
D to 1.1 V	9.494	433.5	4.26×10 ⁻⁶	157.6	3.06×10 ⁻⁵
D to 0.8 V	7.395	487.1	3.36×10 ⁻⁶	141.9	8.21×10 ⁻⁵
D to 0.05 V	9.32	276.4	5.83×10 ⁻⁶	144.1	2.09×10 ⁻⁵
C to 1.8 V	13.79	148.9	6.50×10 ⁻⁶	19.19	6.97×10 ⁻⁶
C to 2.1 V	10.47	143.2	7.52×10 ⁻⁶	13.92	2.93×10 ⁻⁶
C to 3.0 V	12.19	105.6	5.40×10 ⁻⁴	20.99	4.74×10 ⁻⁶

References

- (S1) Y. Pan, X. Cheng, M. Gao, Y. Fu, J. Feng, L. Gong, H. Ahmed, H. Zhang, V. S. Battaglia, ACS Appl. Mater. Interfaces, 2020, **12**, 33621-33630.
- (S2) H. G. Oh, S. H. Yang, Y. C. Kang, S.-K. Park, Int J Energy Res., 2021, **45**, 17738-17748.
- (S3) J. Geng, S. Zhang, E. H. Ang, J. Guo, Z. Jin, X. Li, Y. Cheng, H. Dong, H. Geng, Mater. Chem. Front., 2021, **5**, 6873-6882.
- (S4) B. Wang, X. Miao, H. Dong, X. Ma, J. Wu, Y. Cheng, H. Geng, C. C. Li, J. Mater. Chem. A, 2021, **9**, 14582.
- (S5) B. Li, Y. Liu, X. Jin, S. Jiao, G. Wang, B. Peng, S. Zeng, L. Shi, J. Li and G.

- Zhang, *Small*, 2019, **15**, 1902881.
- (S6) T. Liu, Y. Li, S. Hou, C. Yang, Y. Guo, S. Tian and L. Zhao, *Chem.-Eur. J.*, 2020, **26**, 13716-13724.
- (S7) C. Cui, Z. Wei, G. Zhou, W. Wei, J. Ma, L. Chen and C. Li, *J. Mater. Chem. A*, 2018, **6**, 7088-7098.
- (S8) H. Ge, S. Fan, J. Liu, G. Li, *Energy Technol.* 2021, **9**, 2001074.
- (S9) M. S. Jo, J. S. Lee, S. Y. Jeong, J. K. Kim, Y. C. Kang, D. W. Kang, S. M. Jeong, J. S. Cho, *Small*, 2020, **16**, 2003391
- (S10) S.-K. Park, Y. C. Kang, *ACS Appl. Mater. Interfaces*, 2018, **10**, 17203-17213.
- (S11) S. H. Yang, S.-K. Park, Y. C. Kang, *Chem. Eng. J.*, 2019, **370**, 1008-1018.
- (S12) M. Yousaf, Y. Chen, H. Tabassum, Z. Wang, Y. Wang, A. Y. Abid, A. Mahmood, N. Mahmood, S. Guo, R. P. S. Han, P. Gao, *Adv.Sci.*, 2020, **7**, 1902907.
- (S13) Y. Tang, Z. Zhao, X. Hao, Y. Wang, Y. Liu, Y. Hou, Q. Yang, X. Wang, J. Qiu, *J. Mater. Chem. A*, 2017, **5**, 13591.