Supporting Information

Lithiophilic Flower-like NiO on Cu Foam as 3D Host of for a High-Performance Lithium Metal Batteries

Jiping Ma, Zhanling Zhang , Bin Zhang*, Changyong Huang, Xiaoqian Shi, Yong Liu and Guangmin Zhou*

J. Ma, Prof. Z. Zhang , B. Zhang, C. Huang, X. Shi, Y Liu

School of Materials Science and Engineering, Henan University of Science and Technology, Luoyang 471003, PR China.

J. Ma, Prof. Z. Zhang

Henan Key Laboratory of Nonferrous Materials Science & Processing Technology, Collaborative Innovation Center of Nonferrous Metal, Luoyang 471000, China

Prof. G. Zhou

Shenzhen Geim Graphene Center, Tsinghua-Berkeley Shenzhen Institute, Tsinghua Shenzhen International Graduate School, Tsinghua University, Shenzhen 518055, PR China

Corresponding authors E-mail:

Zhanling Zhang: zzling@haust.edu.cn;

Bin Zhang: zhangbin21@haust.edu.cn

Experimental

Fabrication of the NiO@CF host

Commercial Cu foam (0.4 mm thick) was cut into sheets with a dimension of 32×32 mm^2, then treated in 1 mmol HCl for 2 minutes, and finally cleaned with deionized water and ethanol. 25 mmol urea, 5 mmol $NiCl_2 \cdot 6H_2O$ and 10 mmol NH_4F were added into 50 ml of ultra-pure water and stirred until all of them were dissolved. Then, the completely dissolved solution and the cleaned Cu foam were transferred to a 50 ml reactor and placed into a blast oven to reacted at 120 ℃ for 4 hours. After hydrothermal reaction, the obtained Cu foam was repeatedly washed with ethanol, then dried overnight at 60 ℃ in vacuum, finally annealed at 450 ℃ for 2 h in an inert atmosphere (Ar).

Material Characterization

Scanning electron microscope (SEM, JSM-7800F) was used to study the morphology of the samples and X-ray diffraction (XRD, Bruker D8 Advance) was used to characterize the crystal phase of the samples. The crystal plane spacing of the samples was observed by a high resolution transmission microscope (HRTEM, JEOL JEM-2010F). X-ray photoelectron spectroscopy (XPS, TMO k-alpha) was used to determined the surface composition and chemical states.

Electrochemical Measurement

The contribution of different current collectors to lithium plating/stripping was evaluated by assembling half cells. 2032-type coin cells were assembled CF or NiO@CF was used as the working electrode, commercial Li foil as the counter electrode, Celgard 2500 as the separator, and 1 M LiTFSI in DOL /DME (1 : 1 vol%) solution containing 2% $LiNO_3$ as the electrolyte. The cycling stability and voltage hysteresis of different current collectors was studied by assembling symmetrical cells. Before the symmetrical cell was tested with small current densities (1 and 2 mA cm^{-2}), 10 mAh cm^{-2} lithium was pre-plated on different substrates. When the repeated lithium deposition test was carried out on symmetrical batteries with larger current densities (5, 10 and 15 mA cm^{-2}), we pre-plated 20 mAh cm^{-2} of lithium on different substrates. For the full cells test, $LiFePO_4$ was selected as the cathode, and 10 mAh cm^{-2} lithium was pre-deposited on different substrates as the anode. The full cells were galvanostatically cycled between of 2.5 and 4.2 V at 1 C or 5 C.

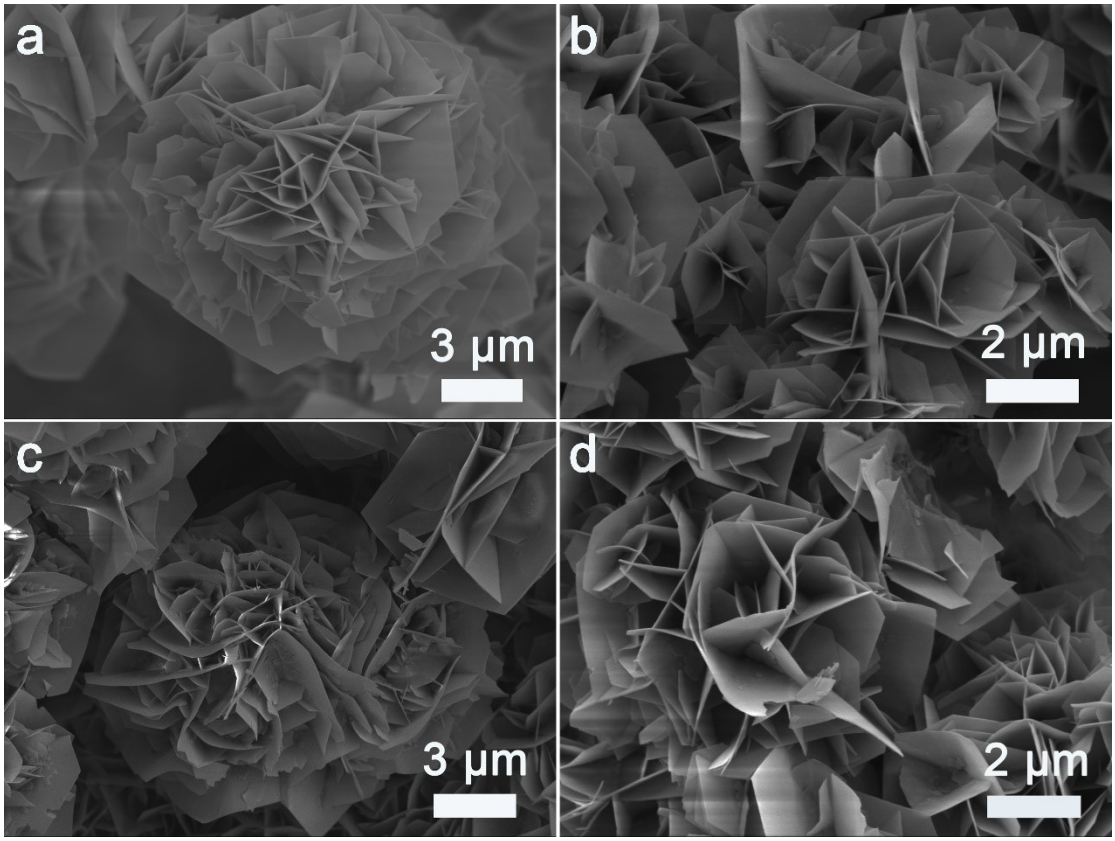

Fig. S1 SEM images after hydrothermal treatment, (a) low magnification, (b) high magnification; SEM images after annealing treatment, (c) low magnification, (d) high magnification

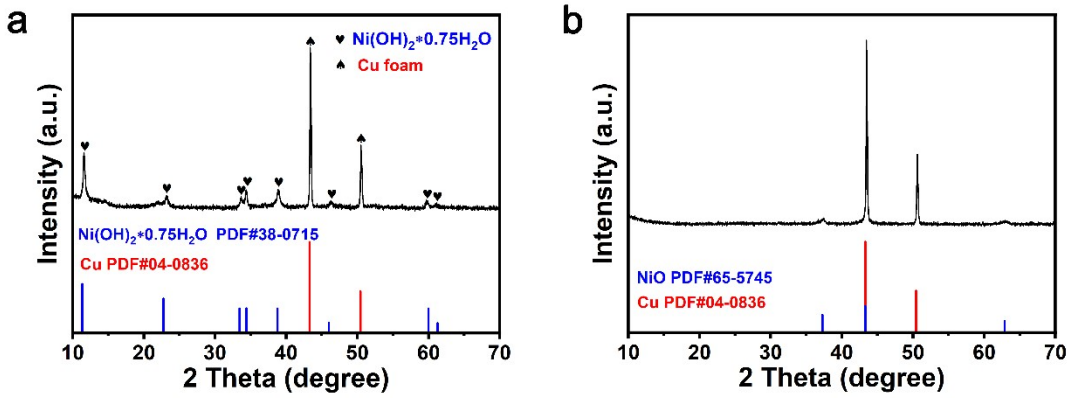

Fig. S2 XRD patterns of (a) $Ni(OH)_2 \cdot 0.75H_2O$@CF, (b) NiO@CF

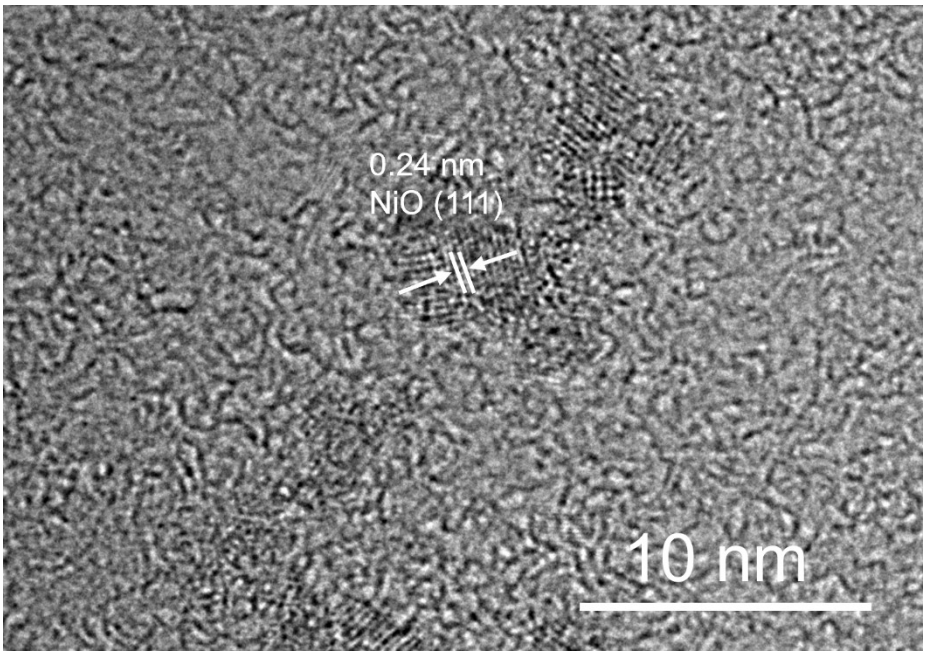

Fig. S3 HR-TEM image of NiO nanosheet

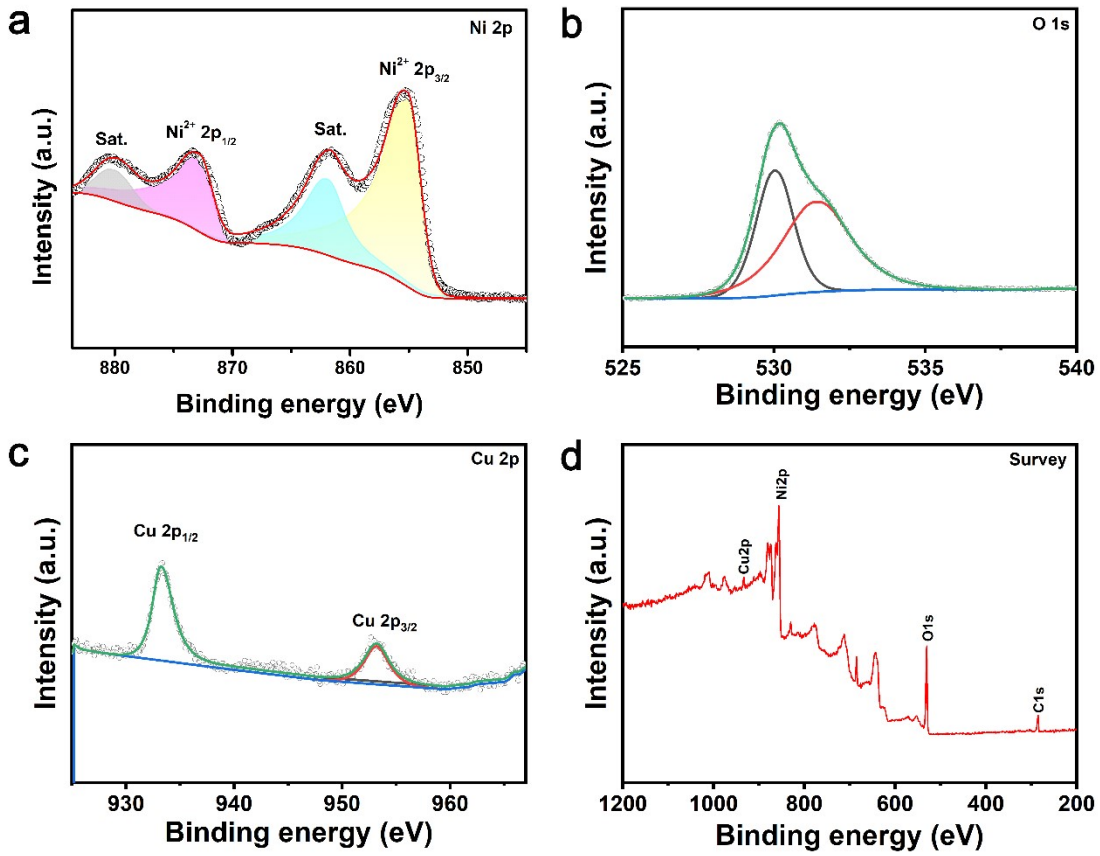

Fig. S4 XPS spectra of NiO@CF. The high-resolution XPS spectrum of (a) Ni 2p, (b) O 1s, (c) Cu 2p, (d) XPS survey spectrum

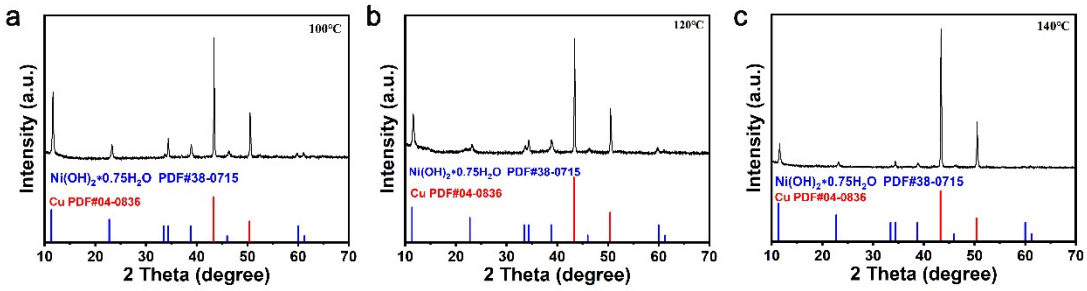

Fig. S5 XRD patterns of $Ni(OH)_2 \cdot 0.75H_2O$/Cu foam composites prepared at different hydrothermal temperatures, (a) 100 ℃, (b) 120 ℃, (c) 140 ℃

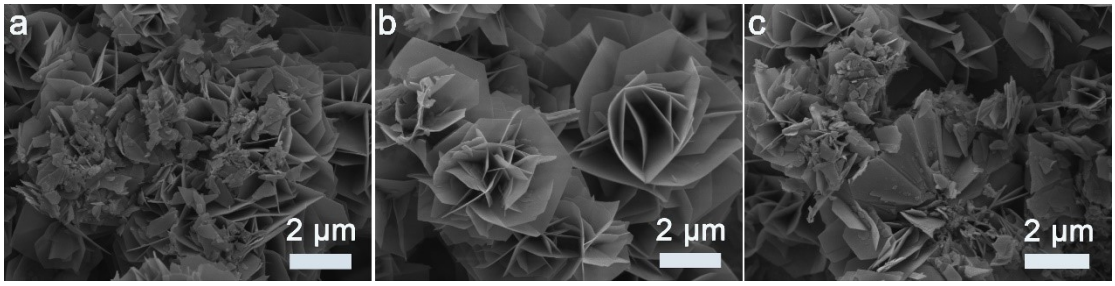

Fig. S6 SEM images of $Ni(OH)_2 \cdot 0.75H_2O$ prepared at different hydrothermal temperatures, (a) 100 ℃, (b) 120 ℃, (c) 140 ℃

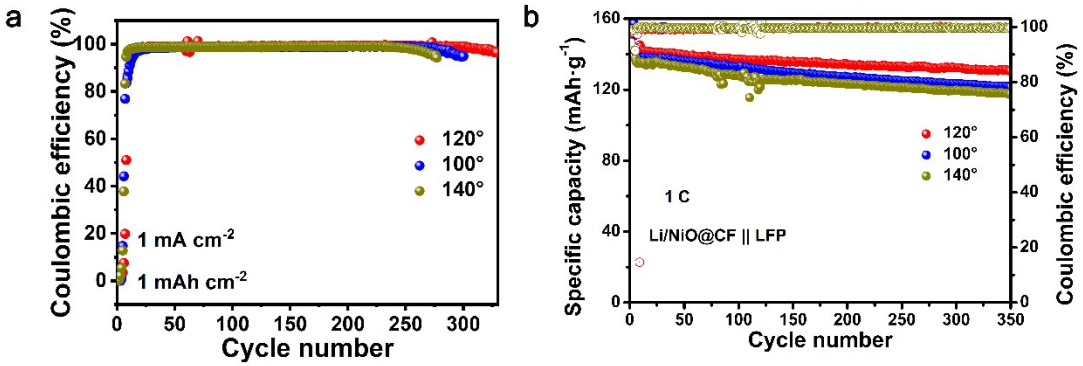

Fig. S7 (a) The coulombic efficiencies of Li || NiO@CF cells, (b) cycling performance of Li/NiO@CF || LFP full battery for NiO@CF eletrodes derived from different hydrothermal temperatures

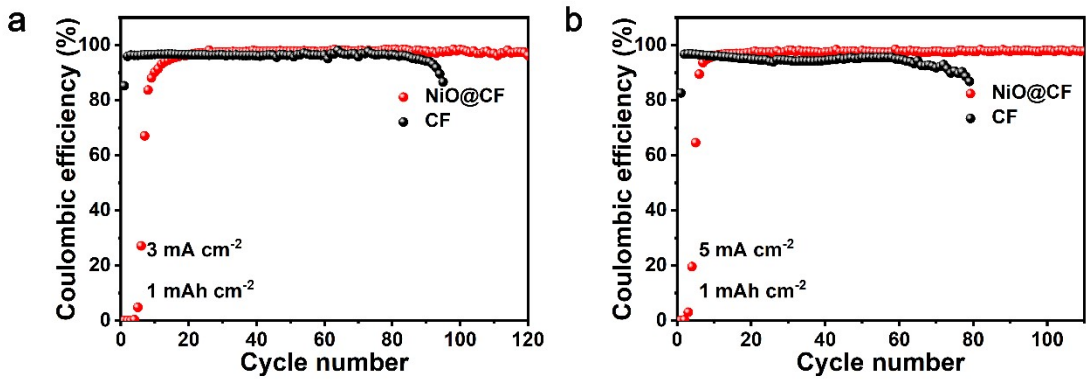

Fig. S8 Coulombic efficiencies comparison of Li || CF and Li || NiO@CF cells tested at a constant deposition capacity of 1 mAh cm^{-2} with different current densities, (a) 3 mA cm^{-2}, (b) 5 mA cm^{-2}

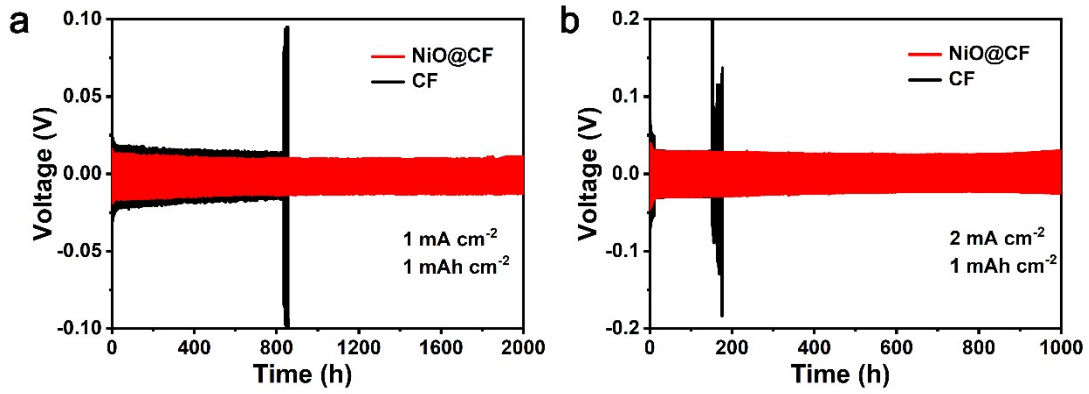

Fig. S9 Electrochemical performance of Li || NiO@CF || Li and bare Li || CF || Li cells tested at different current densities (a) 1 mA cm^{-2}, (b) 2 mA cm^{-2} with a constant areal capacity of 1 mAh cm^{-2}

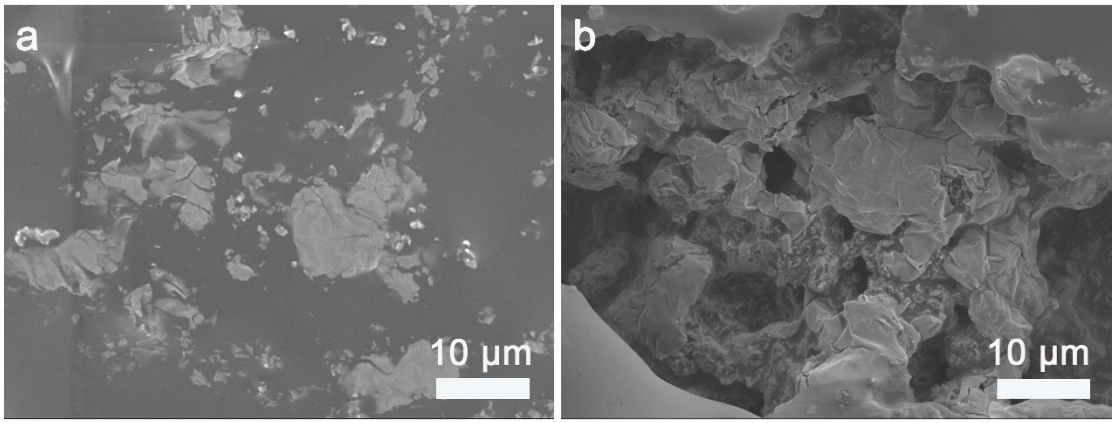

Fig. S10 SEM images of symmetric cells based on NiO@CF and CF anode after cycling 300 h at current density of 10 mA cm^{-2}, with depositing capacity of 10 mAh cm^{-2}, respectively. (a) NiO@CF electrode, (b) CF electrode

Table S1. Comparison table of the symmetric cell data tested at high current density and large area capacity from this work with those reported works

	Current density (mA cm^{-2})	**Area capacity (mAh cm^{-2})**	**Cycle time (h)**	**Reference**
CoO@CF	10	10	600	[1]
NiO nanorrays-Ni	8	10	1000	[2]
NOCA@CF	10	10	400	[3]
Li-NiO/NF	5	1	80	[4]
3D Ni-NiO foam	4	4	200	[5]
(CoO-NiO@CPM)@rGO	1	3	400	[6]
HP-NiO-Ni	0.25	0.5	600	[7]
NiO@CF	**10**	**10**	**1200**	**This work**

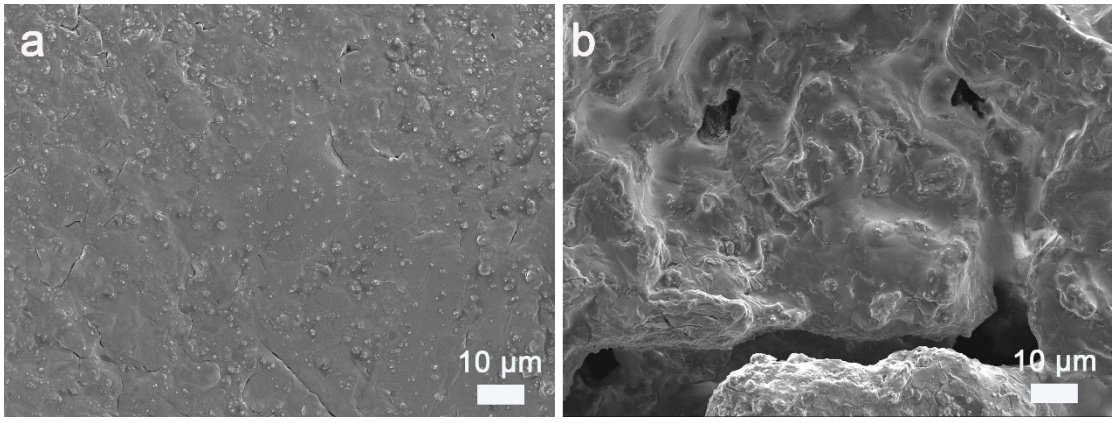

Fig. S11 SEM images of (a) Li/NiO@CF || LFP and (b) Li/CF || LFP full batteries at the anode after cycling 200th at 3 C

Supporting Reference

1. Z. Runhao, L. Yong, W. Meng, L. Dongwei, Z. Junjie, X. Lei, W. Tao, T. Wei, Z. Yanjie, G. Hongyu, G. Meng, L. Kang, C. Pu and K. Biao, *Small*, 2021, **17**, 2101301.
2. L.-M. Wang, Z.-Z. Jin, X.-K. Ban, N.-Z. Li, M.-M. Wang, Q. Shen, Q.-F. Zheng, W. Liu, R.-R. Peng, C.-S. Chen and C.-H. Chen, *J. Electrochem. Soc.*, 2021, **168**.
3. Y. An, Y. Tian, Y. Li, C. Wei, Y. Tao, Y. Liu, B. Xi, S. Xiong, J. Feng and Y. Qian, *Chemical Engineering Journal*, 2020, **400**.
4. Q. Zhang, W.-L. Bai, C.-Y. Sun, X. Liu, K.-X. Wang and J.-S. Chen, *Chem. Eng. J.*, 2021, **405**, 127022.
5. D. Wang, D. Lv, H. Liu, J. Yang, Y. Qian and Z. Chen, *Energy Stor. Mater.*, 2022, **49**, 454-462.
6. W. Wang, K. Wang, Q. Gu, Y. Li, M. Gao, Y. Tao, H. Gong, X. Zhang, X. Jiang and D. Li, *Colloids and Surfaces a-Physicochemical and Engineering Aspects*, 2022, **636**, 128154.
7. W. Lu, C. Wu, W. Wei, J. Ma, L. Chen and Y. Chen, *J. Mater. Chem. A*, 2019, **7**, 24262-24270.