Electronic Supplementary Information for

Engineering yolk-shell P-doped NiS_2/C spheres via MOFs template for high-performance sodium-ion batteries†

Liqin Wang,[a] Zhanli Han,[a] Quanqing Zhao,[a] Xiuyun Yao,[a] Youqi Zhu,*[a] Xilan Ma,[a] Shide Wu,[b] and Chuanbao Cao*[a]

[a] Research Center of Materials Science, Beijing Key Laboratory of Construction Tailorable Advanced Functional Materials and Green Applications, Beijing Institute of Technology, Beijing 100081, China, E-mail: yqzhu@bit.edu.cn (Y. Zhu), cbcao@bit.edu.cn (C. Cao).

[b] Henan Provincial Key Laboratory of Surface and Interface Science, Zhengzhou University of Light Industry, Zhengzhou 450001, China.

Experimental details

Synthesis of Ni-MOFs

In a typical procedure,[1] 0.15 g trimesic acid, 1.0325 g polyvinylpyrrolidone (PVP M=58000, K29-32) and 0.432 g $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in mixed solvent of 15 mL distilled water and 15 mL N,N-dimethylformamide (DMF). After vigorous stirring for 1 h, the homogeneous mixed solution transferred to 50 mL Teflon-lined autoclave and kept in oven under 160 °C for 12 h. The prepared product was washed several times by distilled water and absolute ethanol, and then dried at 80 °C to obtain the yolk-shell Ni-MOFs spheres.

Synthesis of yolk-shell NiS_2 spheres

The 0.1 g Ni-MOFs and 2 g sulfur powder were put in two quartz boats, where the Ni-MOFs and S power were placed at the middle and upstream of the tube furnace, respectively. They were heated under argon atmosphere at 350 °C for 2 h with a heating rate of 1 °C min^{-1}. The final NiS_2 sample with yolk-shell structure was obtained after cooling down to room temperature.

Synthesis of P-doped Ni-MOFs samples

The synthetic procedure was as same as above, 0.15 g trimesic acid, 1.0325 g polyvinylpyrrolidone (PVP M=58000, K29-32) and 0.432 g $Ni(NO_3)_2{\cdot}6H_2O$ were dissolved in mixed solvent of 15 mL distilled water and 15 mL N,N-dimethylformamide (DMF), then added certain amounts of phytic acid (0.01mL, 0.03mL, 0.05 mL and 0.08 mL) with vigorous stirring for 1 h. After transferred to Teflon-lined autoclave and kept at 160 °C for 12 h, the product of P-doped Ni-MOFs samples were collected after washed and dried.

Synthesis of P-doped yolk-shell NiS_2/C spheres

Similarly, the above prepared P-doped Ni-MOFs and sulfur powder were heated in tube furnace by a mass ratio of 1:20 under argon atmosphere at 350 °C for 2 h to acquire P-doped NiS_2/C samples, the NiS_2/C samples with different amount of phytic acid are labeled as 0.01P-doped NiS_2/C, 0.03P-doped NiS_2/C, 0.05P-doped NiS_2/C and 0.08P-doped NiS_2/C, respectively.

Synthesis of NiS_2 particles

0.582 g $Ni(NO_3)_2{\cdot}6H_2O$, 0.5 mL ethylenediamine and 0.8 mL CS_2 were dissolved into 35 mL distilled water. After vigorous stirring for 30 min, the mixed solution transferred to 50 mL Teflon-lined autoclave and maintained at 180 °C for 12 h. Then black sample was washed and dried to

produce NiS_2 particles.

Materials characterization

The crystal phases and crystallinity of synthesized samples were determined by X-ray diffraction (XRD) with PANalytical X-pert diffractometer (Netherlands) using Cu-Kα radiation (λ=0.15418 nm). The valence states of elements on the surface were characterized through X-ray photoelectron spectroscopy (XPS, PHI Quanteral II) with Al Kα source (1486.6 eV). The micromorphologies and elements distribution were surveyed by field-emission scanning electron microscopy (FESEM, Hitachi S-4800) with energy-dispersive X-ray spectroscopy (EDS, EDAX, PW9900). The microstructures and elemental mappings were observed by high-resolution transmission electron microscopy (HRTEM, JSM-2100F) with 200 kV operating voltage. The specific surface area and pore size distribution were measured by the N_2 adsorption-desorption tester (NOVA 4200e, Quantachrome Instruments, USA) employs on the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) model.

Electrochemical test

The electrochemical properties measurements were implemented at room temperature using CR 2025 coin-type cell. The work electrodes consisting of active material, super P and polyvinylidene fluoride (PVDF) in N-Methyl-2-pyrrolidone (NMP) with a mass ration of 7:2:1 were assembled in glovebox, where the concentrations of O_2 and H_2O were limited below 0.01 ppm. The quality of active materials coated on carbon paper (current collector) was roughly 1.5 mg with the areal mass loading of 0.97 mg cm^{-2}. The metallic sodium and Whatman glass fiber were used as the counter electrode and separator, respectively. 1 M $NaClO_4$ dissolved into ethylene carbonate (EC) and dimethyl carbonate (DMC) (1:1 volume ratio) with 5 wt% fluoroethylene carbonate (FEC). The galvanostatic charge and discharge measurements were carried out by using Land battery system (LAND CT2001A) at different current densities of 0.1 to 2 A g^{-1} with the voltage of 0.05-3 V. Cyclic voltammetry (CV) tests were conducted on electrochemical workstation (CHI 660E, Chen-hua) at various sweep speeds of 0.1 to 1 mV s^{-1}. Electrochemical impedance spectroscopy (EIS) was executed on same electrochemical workstation with an appropriate AC voltage amplitude of 5 mV corresponding to frequency range of 10^5-10^{-2} Hz.

Supplementary figures and tables

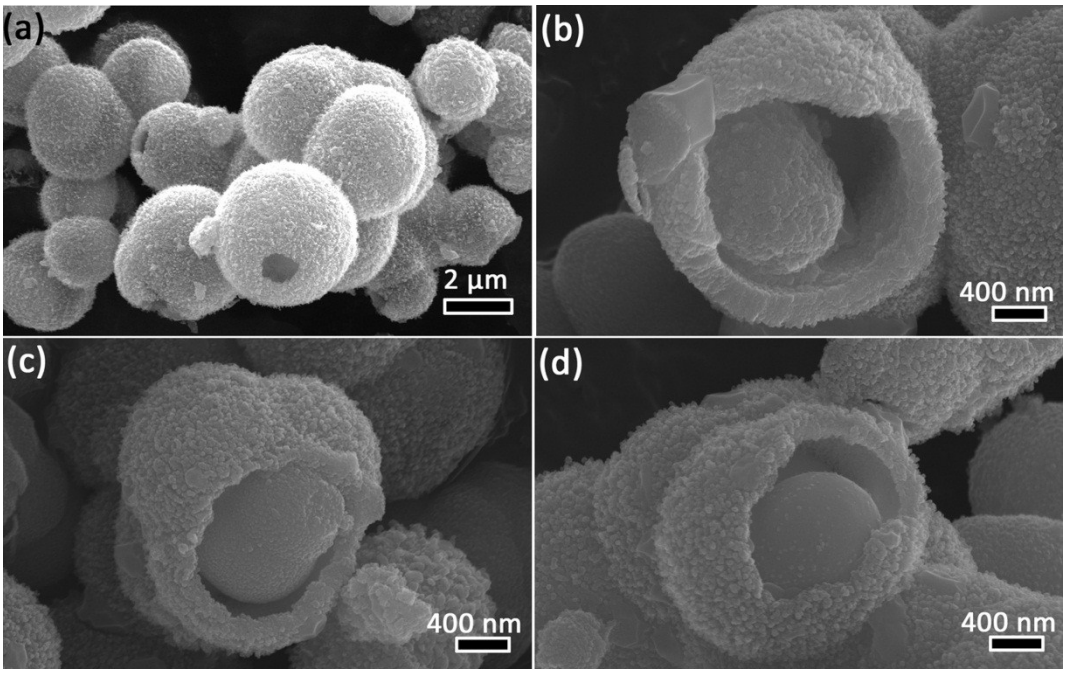

Fig. S1 FESEM images of (a) yolk-shell NiS_2/C spheres, P-doped NiS_2/C spheres with different amount of phytic acid (b) 0.01 mL, (c) 0.05 mL and (d) 0.08 mL.

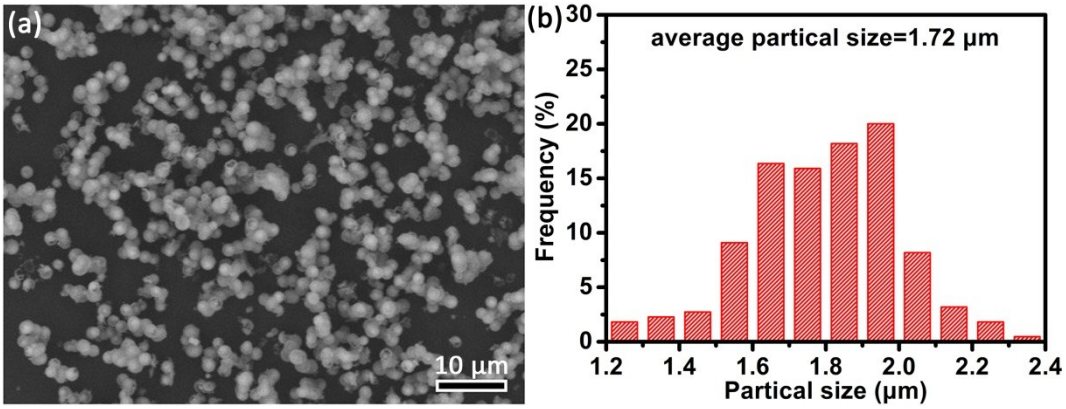

Fig. S2 (a) The low-resolution SEM image and (b) corresponding particle size distribution of 0.03P-doped NiS_2/C sample.

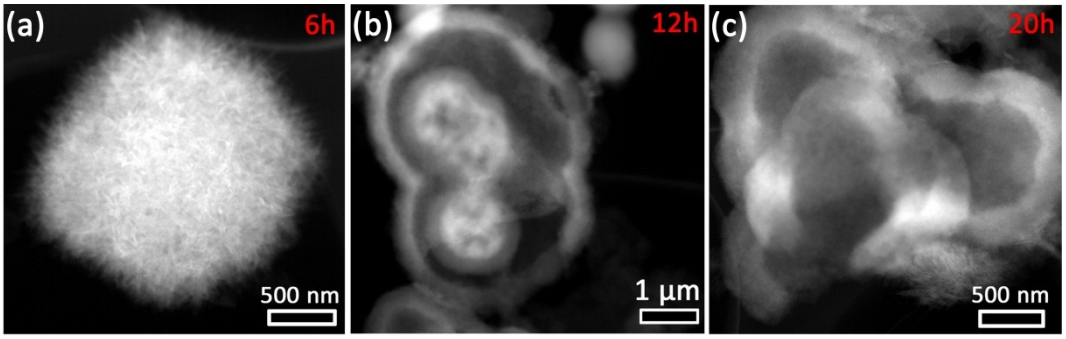

Fig. S3 HAADF-STEM images of corresponding actual morphologies of Ni-MOFs: (a) flower-shaped solid, (b) yolk-shell sphere and (c) hollow sphere.

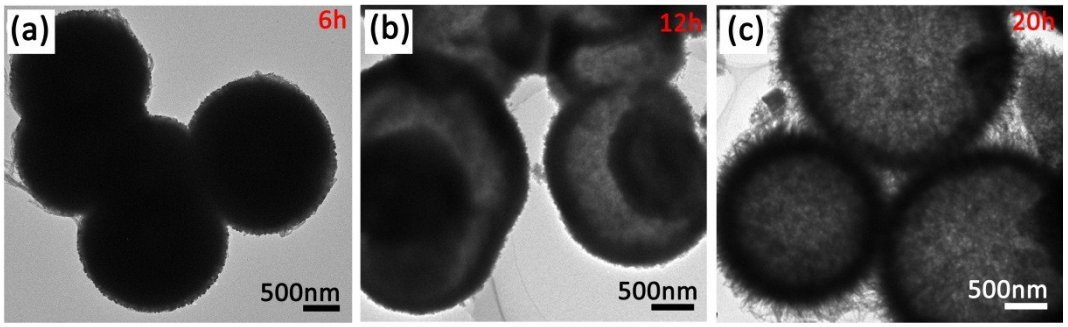

Fig. S4 TEM images of NiS_2 spheres at different synthetic times: (a) solid sphere, (b) yolk-shell sphere and (c) hollow sphere.

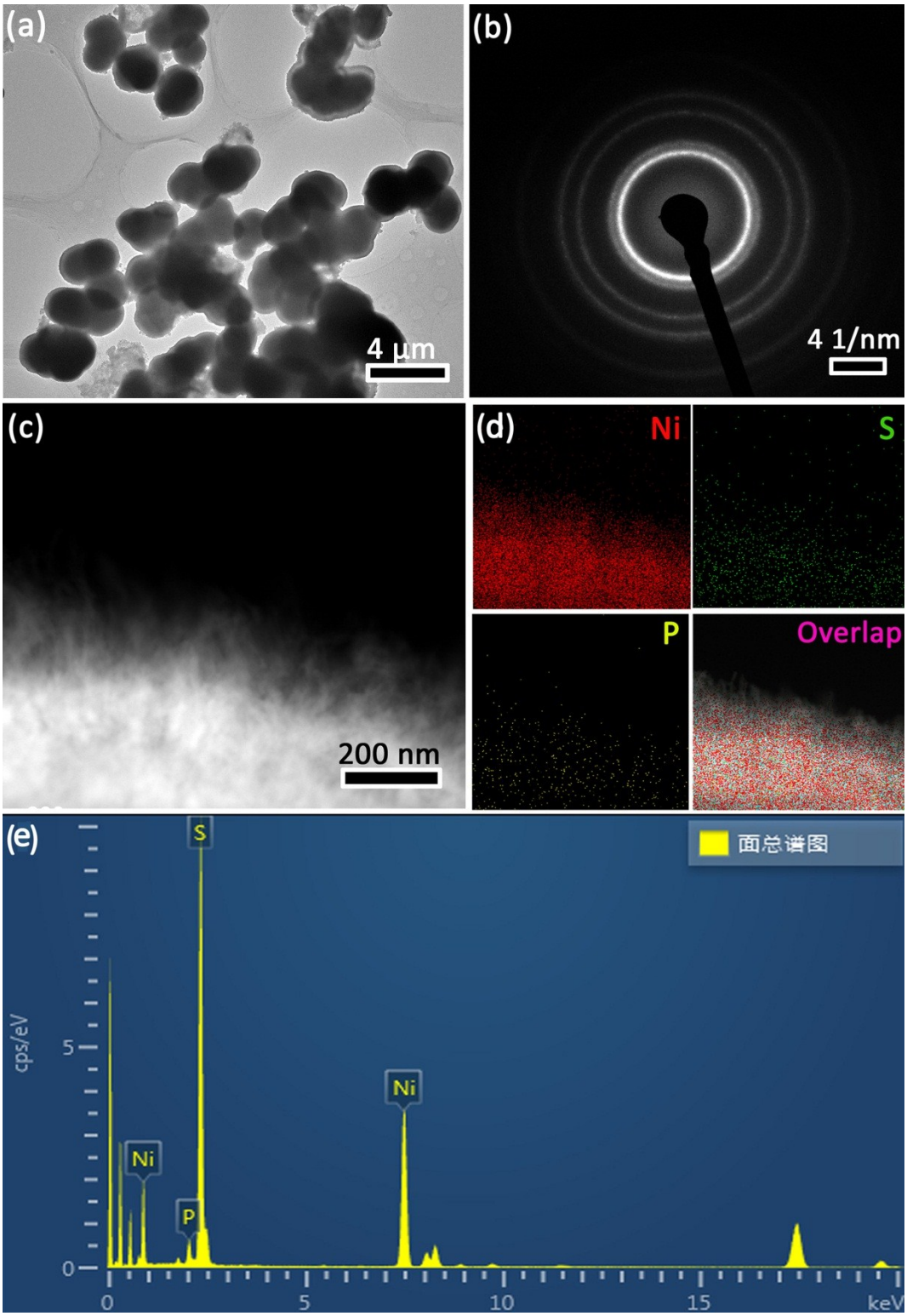

Fig. S5 The low-resolution TEM image (a) and (b) SAED of Ni-MOFs spheres; STEM image (c) of the edge texture and corresponding elemental mapping (d) of Ni, S and P species, and EDS (e) of yolk-shell 0.03P-doped NiS_2/C spheres.

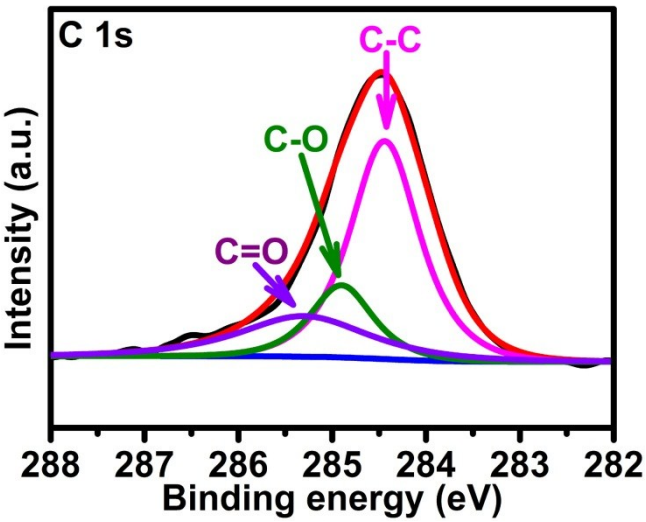

Fig. S6 High-resolution C 1s XPS spectra of 0.03P-doped NiS_2/C spheres.

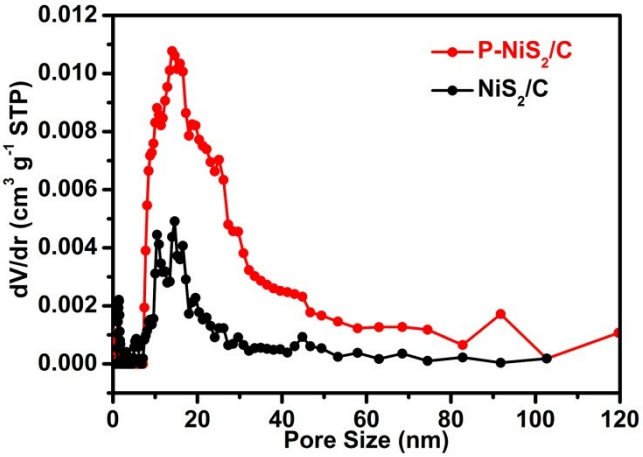

Fig. S7 BJH pore-size distributions of yolk-shell NiS_2/C and 0.03P-doped NiS_2/C spheres.

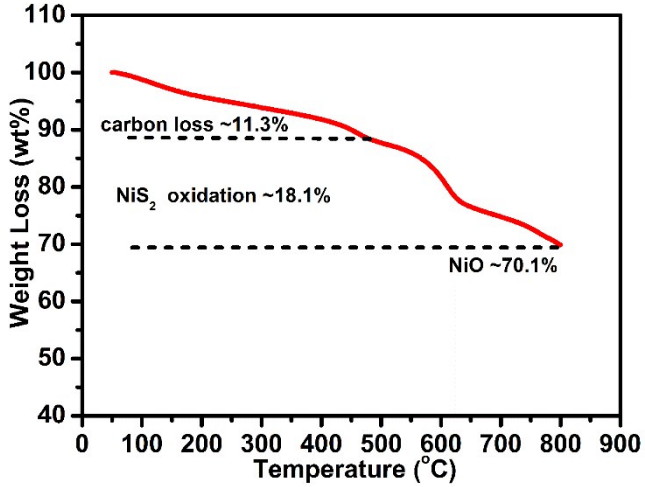

Fig. S8 TGA curve of 0.03P-doped NiS_2/C sample.

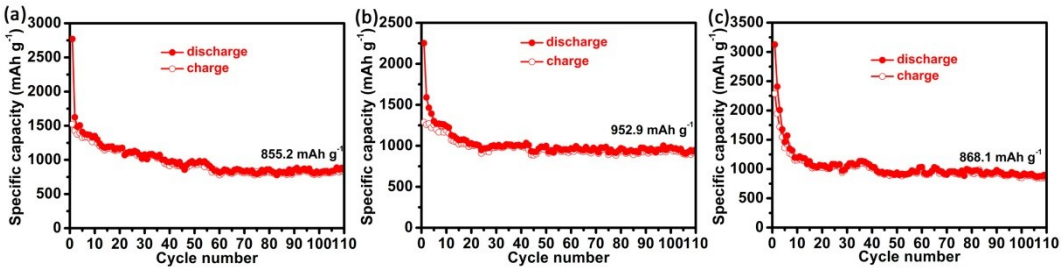

Fig. S9 Cycling performances of (a) 0.01P-doped NiS_2/C spheres, (b) 0.05P-doped NiS_2/C spheres, and (c) 0.08P-doped NiS_2/C spheres at 0.1 A g^{-1} after 110 cycles.

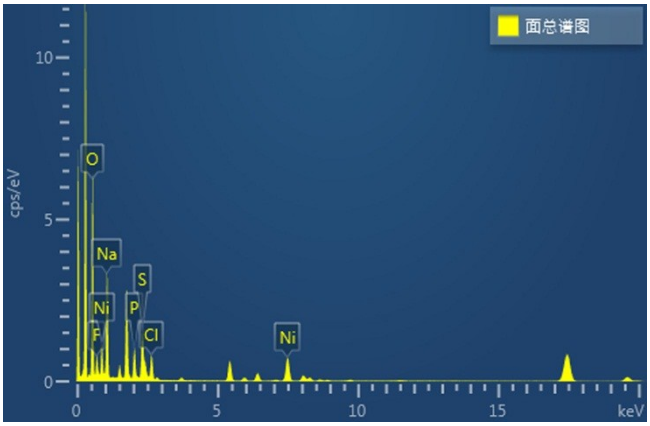

Fig. S10 The corresponding EDS of the long-term cycled 0.03P-doped NiS_2/C spheres.

Table S1 Comparison of sodium storage performances for NiS_X-based materials in previous reported literatures.

materials	current density (A g^{-1})	cycle number	specific capacity (mAh g^{-1})	references
0.03P-doped NiS_2/C	0.1	110	1113.5	our work
0.03P-doped NiS_2/C	0.5	400	766.8	our work
NiS_2/C	0.1	110	706.4	our work
NiS_2-GNS	0.0807	200	407	2
NiS_2	0.1	100	692	3
NiS_2	0.5	1000	319	3
NiS_2	0.1	100	848	1
NiS_2⊂PCF	0.087	100	679	4
NiS_2/NC	0.1	100	505.7	5
NiS_2/NC	0.5	300	356.2	5
NiS_2 NP/p-CNF	0.1	100	500	6
NiS_2@C@C	0.1	100	580.8	9
NiS_x/CNT@C	0.1	200	340	7
Ni_3S_2/C	0.1	100	453	8

Notes and references

1. R. Bi, C. Zeng, H. Huang, X. Wang and L. Zhang, *J. Mater. Chem. A*, 2018, **6**, 14077−14082.
2. R. Sun, S. Liu, Q. Wei, J. Sheng, S. Zhu, Q. An and L. Mai, *Small*, 2017, **13**, 1−8.
3. Q. Chen, S. Sun, T. Zhai, M. Yang, X. Zhao and H. Xia, *Adv. Energy Mater.*, 2018, **8**, 1−9.
4. G. Zhao, Y. Zhang, L. Yang, Y. Jiang, Y. Zhang, W. Hong, Y. Tian, H. Zhao, J. Hu, L. Zhou, H. Hou, X. Ji and L. Mai, *Adv. Funt. Mater.*, 2018, **28**, 1803690.
5. J. Li, J. Li, D. Yan, S. Hou, X. Xu, T. Lu, Y. Yao, W. Mai and L. Pan, *J. Mater. Chem. A*, 2018, **6**, 6595−6605.
6. W. Zhao, S. Ci, X. Hu, J. Chen and Z. Wen, *Nanoscale*, 2019, **11**, 4688−4695.
7. X. Zhao, H.-E. Wang, R.C. Massé, J. Cao, J. Sui, J. Li, W. Cai and G. Cao, *J. Mater. Chem. A*, 2017, **5**, 7394−7402.
8. T. Wang, P. Hu, C. Zhang, H. Du, Z. Zhang, X. Wang, S. Chen, J. Xiong and G. Cui, *ACS Appl. Mater. Interfaces*, 2016, **8**, 7811−7817.
9. F. Zhao, Q. Gong, B. Traynor, D. Zhang, J. Li, H. Ye, F. Chen, N. Han, Y. Wang, X. Sun and Y. Li, *Nano Res.* 2016, **9**, 3162−3170.