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Introduction

With the rapid development of energy storage systems for digital products, electric vehicles and mobile devices, significant attention has been drawn to rechargeable lithium-ion batteries (LIBs). LIBs possess remarkable properties such as high energy density, low cost, and long cycle life compared to other alternatives.^{1–4} In particular, they are considered to be a promising candidate of power sources for future portable electronic devices, electric vehicles and hybrid electric vehicles.^{5,6} Nevertheless, graphite, as a popular material for commercial LIBs, hosts a low theoretical specific capacity (372 mA h g^{-1}) that cannot meet urgent requirements.⁷ Since the first report by Tarascon et al.,⁸ transition metal oxides (TMO) have been considered to be potential anode materials for LIBs in view of their large theoretical specific capacity.⁹⁻¹⁶ As an outstanding representative, Co₃O₄ with an inverse spinel structure has attracted extensive research interest owing to its high theoretical lithium-storage capacity (890 mA h g^{-1}), high corrosion stability, low cost, excellent catalytic properties, and abundance in nature.^{17–19}

Despite these considerable advantages, Co_3O_4 electrodes still face some challenges, such as degradation of capacity and limited rate capability owing to their large volume expansion/ contraction, slow solid-state Li⁺ diffusion, and inferior electronic conductivity during lithiation/de-lithiation processes.^{20,21} To overcome the aforementioned issues, two generally accepted strategies have been utilized including the construction of



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We report on hollow Co_3O_4 cubes synthesized *via* a self-sacrificing template method and their application as an anode material for reversible electrochemical lithium storage. The hollow Co_3O_4 cube with a porous hierarchical structure increases the contact surface, shortens the diffusion path of ion/electron, and improves its structure stability and collaborative electronic transmission. Due to their ultrathin subunits and hollow interior, the electrodes exhibit excellent electrochemical performance. Impressively, a high discharge specific capacity of 1600 mA h g⁻¹ is obtained at 400 mA g⁻¹ after 100 cycles. And a reversible specific capacity of 1032 mA h g⁻¹ could still be maintained even at 1000 mA g⁻¹ after 150 cycles. This implies the remarkable potential as an anode for lithium ion batteries. Thus, the hollow Co_3O_4 cube might give insights into transition-metal oxides as energy storage materials.

electrode materials with designed structures to maintain good structural stability and the introduction of carbon-conducting agents to transfer electrons effectively.^{22–25} Therefore, it is interesting but challenging to design and fabricate Co_3O_4 electrode materials with a stable structure.

Recently, various Co₃O₄ structures have been fabricated and studied extensively, such as the fabrication of nanowires, nanospheres, nanorods, nanotubes, sheets, cages, porous structures, etc.²⁶⁻³⁶ They displayed favorable effects in enhancing the electrochemical properties in LIBs. Among these, the construction of a porous hollow structure, featuring interconnected nano-subunits constituting a hollow interior, has been proved to be an effective way to alleviate the structural strain.³⁷⁻³⁹ It is reported that the particular structure may retard volume expansion, leading to mitigate the destruction of the nanostructure during lithiation/de-lithiation processes.33,40-42 Porous hollow structures guarantee better infiltration of the electrolyte to the electrode, which may enable the acceleration of the ion migration rate during the insertion and deinsertion cycles of the lithium ions. What is more, the nano-subunits can shorten the ion migration distance, resulting in high cycling stability and good rate capability. It should be pointed out that Co₃O₄ with a designed structure may be constructed through the transformation from a precursor to a nanostructured porous phase. Recently, metal organic frameworks (MOFs), as multifunctional materials, have been widely applied as templates or precursors owing to their tunable porosities and functionalities. For example, Co₃O₄ nanoparticles with opened-book morphology derived from MOFs (Co-CPs) exhibited excellent rate capability as anode materials for LIBs.⁴³ By using Co-based MOFs as the sacrificial template, porous Co₃O₄ tetrahedra have been constructed.⁴⁴ Minihollow polyhedron Mn₂O₃, porous Zn_xCo_{3-x}O₄ hollow polyhedron,





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etc. have been synthesized from MOFs and exhibited excellent electrochemical performance.^{45,46}

Herein, we report on a facile and scalable method to construct hollow Co₃O₄ cubes *via* a self-sacrificing template method. The low-cost benzimidazole was firstly adopted to serve as the ligand. The precursors provided some superiority related to their robust morphology. The resulting Co₃O₄ inherited the cubic morphology of the precursors, while the hollow structure may be attributed to the thermal treatment of organic parts in the precursors. This approach is simple, tunable, and scalable. When applied as anode materials in LIBs, the as-synthesized hollow Co₃O₄ cube exhibits high reversible lithium storage capacity, excellent cyclic stability, and good rate capability. A reversible specific capacity of about 1600 mA h g^{-1} is maintained after 100 cycles at 400 mA g^{-1} . Importantly, the hollow Co₃O₄ cube electrode not only shows high capacity even at high rates, but also demonstrates good cyclic stability. A discharge specific capacity of 1215 mA h g^{-1} is retained when the rate is increased to 3200 mA g^{-1} . This indicates the potential application of hollow Co3O4 cubes as anode materials for LIBs. The hollow Co₃O₄ cube structure with a fast lithium ion diffusion and a high electrode-electrolyte contact area may be beneficial for the maximum utilization of electrochemically active Co₃O₄ as energy storage materials.

Experimental

Materials preparation

A hydrothermal method was adopted to synthesize the Coprecursor. DI water was used throughout the experiment. In a typical synthesis, 5 mmol Co(CH₃COO)₂·4H₂O (99.5%) and 2.5 mmol benzimidazole (98.0%) were dissolved in a mixed solution of 20 ml iso-propyl alcohol (IPA) and 20 ml DI water to form a settled solution. The settled solution was then transferred into a 50 ml Teflon-lined stainless autoclave, and kept at 180 °C for 6 h in an oven. After the reaction, the light pink precipitates were harvested and washed with distilled water and ethanol several times, then dried at 80 °C for 6 h. The dried precipitate was heat-treated at 400 °C for 2 h with a heating rate of 2 °C min⁻¹ in air to obtain the hollow Co₃O₄ cube.

Materials characterizations

Crystallographic information was acquired using powder X-ray diffraction (XRD, D8 Advance diffractometer, Bruker) by applying Cu K_{α} irradiation. The microstructures of the samples were observed by scanning electron microscopy (SEM, FEI Quanta 250 FEG) and transmission electron microscopy (TEM, JEM-2010F, JEOL). Raman spectra were recorded on a Thermo Scientific Raman Microscope DXR with a 532 nm laser excitation length. The N₂ adsorption–desorption isotherms were examined using a Quantachrome ASIQC-4 instrument. Thermogravimetric analysis (TGA) was performed on a Mettler Toledo TGA/DSC1.

Electrochemical measurements

The electrochemical measurements were conducted on a cointype half-cell (CR 2025). The working electrodes were assembled as follows. Briefly, the as-prepared active materials, acetylene black and sodium carboxymethyl cellulose (CMC) were mixed in a mass ratio of 80:10:10 and dispersed in deionized water. Then the slurry was pasted on a Cu foil using a spatula and dried at 60 °C overnight under vacuum. Metallic lithium was used as the counter electrode, and a Cegard 2400 film was used as a separator. The electrolyte was 1 M LiPF₆ in a 1:1 (volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC). The cycling tests of porous hollow Co₃O₄ were run at different current densities using a LAND CT2001 (LAND electronics Co., Ltd, China) cell test system in the voltage range of 0.01–3.0 V (*vs.* Li⁺/Li). Cyclic voltammetry (CV) was performed using a Zahner/Zennium electrochemical workstation.

Results and discussion, experimental

Fig. 1 shows a typical well-defined cube for Co-precursors with sizes of 5-10 µm. A single cubic structure with smooth surface is further observed using a magnified FESEM image (Fig. 1b). Interestingly, configurations similar to those of the Co-precursors and some cubic structures were perfectly inherited in the calcined products (Fig. 2a and b), but with rough surfaces and hollow structures in comparison with the precursor (Fig. 1). The observations with different magnifications (Fig. 2c) further prove that the surface of the hierarchical cubic structures is constructed from numerous nanosheets. The rough surface of Co₃O₄ should be attributed to the massive loss of inner organic contents. As depicted in Fig. 2d using TEM, a more detailed observation confirms that the as-obtained Co₃O₄ with a rough surface is a hollow structure. The hollow structures and inner cavities of the hollow Co₃O₄ cube are clearly illustrated by the distinct contrast between the center and the edge. The ultrathin nanosheets are composed of numerous spherical subunits, with a narrow size distribution, i.e., most of them are 10-20 nm in diameter (Fig. 2e). The thickness of the ultrathin nanosheet subunits is about 10 nm. Also well-dispersed nanopores formed between the subunits are observed (as circled in Fig. 2e). The high-resolution transmission electron microscopy (HRTEM) image (Fig. 2f) shows the crystal lattice fringes with an interlayer distance of 0.24 nm, which is in accordance with the (311) plane of Co_3O_4 with a cubic structure. The selected area electron diffraction (SAED) pattern exhibits the polycrystalline structure of the hollow Co₃O₄ cube (inset, Fig. 2f).

Their phase purity and composition of the hollow Co₃O₄ cube were checked using X-ray diffraction (XRD), as depicted



Fig. 1 SEM images of the Co-precursors.



Fig. 2 (a-c) SEM images of the as-obtained hollow Co_3O_4 cube at different magnifications; (d) TEM and (e and f) HRTEM images of Co_3O_4 at different magnifications; inset (f): indexed SAED pattern of Co_3O_4 .



Fig. 3 (a) XRD patterns of the hollow Co_3O_4 cube and standard of Co_3O_4 from JCPDS card 42-1467; (b) Raman spectrum of the hollow Co_3O_4 cube; (c) XPS spectra of Co 2p for the Co_3O_4 sample; and (d) TGA-DSC results of the precursor (10 °C min⁻¹ in air).

in Fig. 3a. The peaks at 19.1, 31.5, 37.0, 38.7, 44.9, 55.7, 59.5, and 65.3 degrees belong to the (111), (220), (311), (222), (400), (422), (511), and (440) lattice planes of the face centered cubic (fcc) phase of Co_3O_4 (JCPDS No. 42-1467), respectively. This indicates that the precursor was completely transformed into

 Co_3O_4 and no peaks could be assigned to other crystal phases. In the Raman spectrum of the as-synthesized Co_3O_4 cube (Fig. 3b), four bands located at 468, 512, 604, and 668 cm⁻¹ are observed, which correspond to the Eg, F_{2g}, F_{2g}, and A_{1g} modes of the spinel Co_3O_4 phase, respectively.⁴⁷ This further proves that the as-synthesized material is pure Co_3O_4 without any impurities.

The valences of Co in the Co₃O₄ cube were detected by X-ray photoelectron spectroscopy (XPS), as depicted in Fig. 3c. In the high-resolution Co 2p spectrum, the peaks observed at 779.3 and 794.5 eV can be assigned to the Co 2p_{3/2} and Co 2p_{1/2} spinorbit peaks of Co₃O₄, respectively.^{48,49} In addition, it also shows two extra satellite peaks, which are attributed to the Co^{2+} oxidation state, indicating the presence of both Co²⁺ and Co³⁺ species. To obtain the calcination temperature to convert the precursor into Co₃O₄, TGA-DSC was carried out on the precursor in air (Fig. 3d). A slight mass loss appears before 300 °C, which may be due to the desorption of some guest molecules in the pores of the precursor.³⁹ It is believed that the precursor material decomposes exothermically to Co₃O₄ between 300 and 400 °C. To guarantee the complete decomposition of the precursor, we selected 400 °C as the final calcining temperature. Furthermore, the surface area of the Co₃O₄ cube is about 28 m² g⁻¹ (Fig. 4).

Fig. 5 illustrates the formation process of a porous hollow Co_3O_4 cube. This is due to the synergistic effects of the generated gas release and the Kirkendall effect. We can deduce that vacancies may be formed at the start of the oxidation processes, which take on the reaction interface of the internal precursor and oxygen gas.³⁷ As a result, hollow cavities are formed. Meanwhile, pores connected to each other derive from the released gas during the oxidation processes. Thus, the hollow Co_3O_4 cube with porous shells is achieved.



Fig. 4 (a) Nitrogen adsorption–desorption isotherms and (b) BJH pore size distribution plots of the hollow Co_3O_4 cube electrode.



Fig. 5 Schematic illustration of the formation of the hollow Co_3O_4 cube.



Fig. 6 (a) Cyclic voltammograms of the hollow Co_3O_4 cube electrode in the initial 5 cycles at a rate of 0.1 mV s⁻¹. (b) Discharge/charge curves of hollow Co_3O_4 cube electrodes at different cycles. (c) Discharge capacity of hollow Co_3O_4 cube electrodes for the first 100 cycles at 400 mA g⁻¹. (d) Rate performance of hollow Co_3O_4 cube electrodes tested between 0.01 and 3.0 V.

Hollow Co₃O₄ cubes were prepared via self-sacrificial template method, and used as anodes in LIBs. Cyclic voltammetry (CV) curves of the hollow Co₃O₄ cube in the potential widow of 0.01–3.0 V at a scan rate of 0.1 mV s^{-1} for the initial five cycles are presented in Fig. 6a. An irreversible cathodic peak at 0.92 V vs. Li⁺/Li in the first discharge process is clearly identified, which is in accord with the reduction of Co_3O_4 to Co^0 , and the formation of the solid electrolyte interface (SEI) and amorphous Li₂O. In the subsequent cathodic scans, one prominent peak is observed at 1.06 V accompanied by as light peak at 2.17 V, which are attributed to the multistep reduction reactions of Co₃O₄ with Li⁺. From the second cycle onwards, the cathodic peaks almost remain stable. This indicates that the electrochemical reversibility is gradually established. However, the anodic sweeps show an oxidation peak at 2.08 V, which corresponds to the oxidation process of Co⁰ to Co₃O₄ and the decomposition of Li₂O.

Fig. 6b shows the galvanostatic charge-discharge curves of the hollow Co₃O₄ cube electrode in the voltage range of 0.01–3 V versus Li^+/Li at a current density of 400 mA g⁻¹. The first discharge process is depicted along the voltage plateau at 1.08 V followed by a sloping curve down to 0.01 V, which is consistent with previous reports.²³ The initial discharge and charge specific capacities are 1601 and 1282 mA h g⁻¹, respectively, corresponding to a coulombic efficiency of 80%. The capacity loss of 20% may be due to the SEI film originated from the decomposition of the electrolyte. In the next cycles, no discriminable plateau is observed, which may be owing to a heterogeneous reaction mechanism for lithiation/delithiation processes.40,50 In the 2nd cycle, the discharge specific capacity can reach about 1334 mA h g⁻¹. A discharge specific capacity of 1700 mA h g⁻¹ can be maintained after 50 cycles with a coulombic efficiency value of about 100% (Fig. 6b and c).

Fig. 6c displays the cycling performances of the hollow Co_3O_4 cube electrode at 400 mA g⁻¹. For comparison, commercial Co_3O_4 with the sizes of about 200–600 nm (Fig. S1, ESI[†])

was tested under the same current density. Impressively, a reversible specific capacity of 1334 mA h g⁻¹ with a coulombic efficiency of about 100% at the second cycle is obtained for the hollow Co₃O₄ cube anode material. The capacity of the Co₃O₄ electrode gradually increases in the initial 40 cycles. The gradually increasing capacity has been explained by the reversible formation of a polymeric gel-like film deriving from kinetic activation in the hollow Co₃O₄ cube.^{51,52} The capacity is almost constant after 40 cycles and the coulombic efficiency is maintained at about 100%. After 100 cycles, a discharge specific capacity of about 1600 mA h g^{-1} is retained with a coulombic efficiency close to 100%, exhibiting the excellent cycling stability (Fig. 6b and c). In contrast, the commercial Co_3O_4 electrode exhibits a dramatic decrease of discharge specific capacity from 1125 mA h g^{-1} to 275 mA h g^{-1} after 100 cycles. In the 1st cycle, an inferior coulombic efficiency of 41% (Fig. S2, ESI⁺) is obtained. The obtained discharge specific capacity of the hollow Co₃O₄ cube is higher than the theoretical specific capacity of Co_3O_4 (890 mA h g⁻¹). Furthermore, such an outstanding cycling performance of the hollow Co₃O₄ cube is also superior to some reported literatures, such as for hollow Co₃O₄ parallelepipeds,²⁵ 3D hierarchical Co₃O₄ microspheres,²⁷ nanocage Co_3O_4 ³¹ and even some Co_3O_4 /grapheme²⁴ composites. The extra capacity may be attributed to pseudocapacitive contribution, reversible decomposition and formation of the SEI film, and enhanced lithium storage in the interface, surface, and pores of the hollow Co₃O₄ cube.⁵³⁻⁵⁸

The rate capability of the hollow Co_3O_4 cube was tested. The highest discharge capacity of 1550 mA h g⁻¹ is achieved at 200 mA g⁻¹. As demonstrated in Fig. 6d, the 5th cycle discharge capacities are 1341, 1386, 1417, 1389, 1324 and 1215 mA h g⁻¹ at 200, 400, 800, 1400, 2200 and 3200 mA g⁻¹, respectively. As the rate returned to 200 mA g⁻¹ from 3200 mA g⁻¹, the capacity recovers to 1290 mA h g⁻¹ and increases to 1640 mA h g⁻¹ after 35 cycles, which is more higher than the initialization. This indicates that the hollow Co_3O_4 cube can tolerate changes of high rates. The discharge potential decreased gradually with an increase in current density (Fig. S3, ESI†). The voltage polarization was very small even at a high rate of 3200 mA g⁻¹, demonstrating good reaction kinetics of the hollow Co_3O_4 cube.

Fig. 7 shows the cycling performance of the hollow Co_3O_4 cube electrode at 1000 mA g⁻¹. It is noticed that the hollow Co_3O_4 cube electrode delivers a specific capacity of 1032 mA h g⁻¹ (with 68% capacity retention) after 150 cycles, implying its suitability for high rate applications. The extra capacity could be mainly attributed to the reversible formation of a polymeric gel-like film caused by electrolyte degradation.^{51,52} The coulombic efficiency is nearly 100% after the second cycle, indicating the outstanding reversible Li⁺ insertion/extraction ability of the hollow Co_3O_4 cube electrode.

To further explain the improved electrochemical properties of the hollow Co_3O_4 cube, the morphology of Co_3O_4 electrodes after 50 cycles was obtained (Fig. 8). No obvious morphology change was observed, despite a certain deformation during the Li⁺ insertion/extraction processes. The hollow interior and small size-distribution of subunits are maintained after cycling. This demonstrates that a robust hollow Co_3O_4 cube can effectively



Fig. 7 Cycling performance of the porous hollow ${\rm Co}_3{\rm O}_4$ electrode at 1000 mA g^{-1}



Fig. 8 SEM image of the hollow Co $_3\text{O}_4$ cube electrode after 50 cycles at 400 mA $g^{-1}.$

accommodate the large volume change during lithiation/ delithiation. Hence, it is believed that the enhanced cycling and rate performances are related to the unique nanostructure of the hollow Co_3O_4 cube, primarily due to the following factors. (i) The hollow and porous structures are beneficial for the electrolyte diffusion and lithiation/delithiation processes. (ii) The hollow and porous structures could effectively offer a buffer space to tolerate the volume expansion/contraction of Co_3O_4 and maintain structural stability during lithiation/delithiation. (iii) Owing to the ultrathin subunits, the porous hollow Co_3O_4 cube could afford extra active sites for the surface storage of Li⁺ and shorten the Li⁺ diffusion route. We believe that the combination of special nanostructures leads to the increased electrochemical performances of the porous hollow Co_3O_4 material.

Conclusions

In summary, hollow Co_3O_4 cubes were prepared *via* a self-sacrificing template method. The low-cost benzimidazole was

firstly adopted to serve as the ligand. When evaluated as an anode material for LIBs, the hollow Co_3O_4 cube exhibited a large lithiumstorage capacity, superior rate capability up to 3200 mA g⁻¹, and good cyclic stability (1600 mA h g⁻¹ at 400 mA g⁻¹ after 100 cycles). The improved electrochemical performance of the Co_3O_4 cubes profits from their highly porous hollow structure. This is beneficial for the diffusion of the electrolyte and insertion/extraction of Li⁺, and buffers the large volume expansion/contraction of materials during the lithiation/delithiation processes. These results display that the hollow Co_3O_4 cube is a promising candidate as a next-generation LIB anode material.

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Notes and references

- 1 M. Winter and R. J. Brodd, *Chem. Rev.*, 2004, **104**, 4245-4269.
- 2 D. W. Song, P. Y. Hou, X. Q. Wang, X. X. Shi and L. Q. Zhang, *ACS Appl. Mater. Interfaces*, 2015, 7, 12864–12872.
- 3 F. Lin, I. M. Markus, D. Nordlund, T. C. Weng, M. D. Asta, H. L. Xin and M. M. Doeff, *Nat. Commun.*, 2014, 5, 4529.
- 4 C. Y. Liu, E. I. Gillette, X. Y. Chen, A. J. Pearse, A. C. Kozen, M. A. Schroeder, K. E. Gregorczyk, S. B. Lee and G. W. Rubloff, *Nat. Nanotechnol.*, 2014, 9, 1031.
- 5 B. Kang and G. Ceder, Nature, 2009, 458, 190-193.
- 6 F. Y. Cheng, J. Liang, Z. L. Tao and J. Chen, *Adv. Mater.*, 2011, 23, 1695–1715.
- 7 J. J. Zhang, T. Huang and A. S. Yu, *J. Power Sources*, 2015, 273, 894–903.
- 8 G. Z. Fang, J. Zhou, Y. S. Cai, S. N. Liu, X. P. Tan, A. Q. Pan and S. Q. Liang, *J. Mater. Chem. A*, 2017, DOI: 10.1039/ c7ta01961k.
- 9 X. Y. Zhao, X. Bai, W. Yang, D. Shen, H. Yang, N. Lun, Y.-X. Qi and Y. J. Bai, *New J. Chem.*, 2016, **40**, 9986–9992.
- J. Jiang, Y. Y. Li, J. P. Liu and X. T. Huang, *Nanoscale*, 2011, 3, 45–58.
- 11 M. V. Reddy, G. V. Subba Rao and B. V. R. Chowdari, *Chem. Rev.*, 2013, **113**, 5364–5457.
- 12 B. Wang, S. M. Li, X. Y. Wu, J. H. Liu, W. M. Tian and J. Chen, New J. Chem., 2016, 40, 2259–2267.
- 13 S. W. Zhang, Q. H. Fan, H. H. Gao, Y. S. Huang, X. Liu, J. X. Li, X. J. Xu and X. K. Wang, *J. Mater. Chem. A*, 2016, 4, 1414–1422.
- 14 N. N. Huo, Y. H. Yin, W. F. Liu, J. Zhang, Y. M. Ding, Q. X. Wang, Z. P. Shi and S. T. Yang, *New J. Chem.*, 2016, 40, 7068–7074.
- 15 V. Sridhar and H. Park, New J. Chem., 2017, 41, 442-446.
- 16 Y. Feng, X. Y. Yu and U. Paik, *Chem. Commun.*, 2016, 52, 6269–6272.

- 17 C. Cheng, G. Zhou, J. Du, H. M. Zhang, D. Guo, Q. H. Li, W. F. Wei and L. B. Chen, *New J. Chem.*, 2014, 38, 2250–2253.
- 18 Y. Hou, J. Y. Li, Z. H. Wen, S. M. Cui, C. Yuan and J. H. Chen, *Nano Energy*, 2015, **12**, 1–8.
- 19 Y. L. Zhang, Y. Li, J. Chen, P. P. Zhao, D. G. Li, J. C. Mu and L. P. Zhang, *J. Alloys Compd.*, 2017, **699**, 672–678.
- 20 Y. Li, B. Tan and Y. Wu, Nano Lett., 2008, 8, 265-270.
- 21 D. Y. Zhao, Q. Hao and C. X. Xu, *Electrochim. Acta*, 2016, **211**, 83–91.
- 22 G. Y. Huang, S. M. Xu, S. S. Lu, L. Y. Li and H. Y. Sun, ACS Appl. Mater. Interfaces, 2014, 6, 7236–7243.
- 23 D. Gu, W. Li, F. Wang, H. Bongard, B. Spliethoff,
 W. Schmidt, C. Weidenthaler, Y. Y. Xia, D. Y. Zhao and
 F. Schüth, *Angew. Chem.*, 2015, 127, 1–6.
- 24 J. M. Xu, J. S. Wu, L. L. Luo, X. Q. Chen, H. B. Qin, V. Dravid,
 S. Mi and C. L. Jia, *J. Power Sources*, 2015, 274, 816–822.
- 25 Y. Han, M. L. Zhao, L. Dong, J. M. Feng, Y. J. Wang, D. J. Li and X. F. Li, *J. Mater. Chem. A*, 2015, **3**, 22542–22546.
- 26 Z. C. Zhang, L. Li, Q. Xu and B. Q. Cao, *RSC Adv.*, 2015, 5, 61631–61638.
- 27 G. X. Pan, X. H. Xia, F. Cao, J. Chen and Y. J. Zhang, *J. Power Sources*, 2015, 293, 585–591.
- 28 L. Wang, B. Liu, S. Ran, H. Huang, X. Wang, B. Liang, D. Chen and G. Shen, *J. Mater. Chem.*, 2012, 22, 23541–23546.
- 29 N. Du, H. Zhang, B. Chen, J. Wu, X. Ma, Z. Liu, Y. Zhang, D. Yang, X. Huang and J. Tu, *Adv. Mater.*, 2007, **19**, 4505–4509.
- 30 Z. P. Li, X. Y. Yu and U. Paik, *J. Power Sources*, 2016, **310**, 41–46.
- 31 Y. Wang, B. F. Wang, F. Xiao, Z. G. Huang, Y. J. Wang, C. Richardson, Z. X. Chen, L. F. Jiao and H. T. Yuan, *J. Power Sources*, 2015, **298**, 203–208.
- 32 G. P. Kim, S. Park, I. Nam, J. Park and J. Yi, *J. Mater. Chem. A*, 2013, **1**, 3872–3876.
- 33 L. Peng, Y. Y. Feng, Y. J. Bai, H. J. Qiu and Y. Wang, J. Mater. Chem. A, 2015, 3, 8825–8831.
- 34 F. M. Zhan, B. Y. Geng and Y. J. Guo, *Chem. Eur. J.*, 2009, 15, 6169–6174.
- 35 M. J. Jing, M. J. Zhou, G. Y. Li, Z. G. Chen, W. Y. Xu, X. B. Chen and Z. H. Hou, *ACS Appl. Mater. Interfaces*, 2017, 9, 9662–9668.
- 36 H. R. Du, C. Yuan, K. F. Huang, W. H. Wang, K. Zhang and B. Y. Geng, J. Mater. Chem. A, 2017, 5, 5342–5350.
- 37 B. Wang, H. Wu, L. Zhang and X. W. Lou, Angew. Chem., Int. Ed., 2013, 52, 4165–4168.
- 38 X. Y. Yu, L. Yu, H. B. Wu and X. W. Lou, Angew. Chem., Int. Ed., 2015, 54, 5331–5335.

- 39 J. Y. Wang, N. L. Yang, H. J. Tang, Z. H. Dong, Q. Jin, M. Yang, D. Kisailus, H. J. Zhao, Z. Y. Tang and D. Wang, *Angew. Chem., Int. Ed.*, 2013, **52**, 6417–6420.
- 40 L. Hu and Q. Chen, Nanoscale, 2014, 6, 1236-1257.
- 41 M. E. Im, D. Pham-Cong, J. Y. Kim, H. S. Choi, J. H. Kim, J. P. Kim, J. Kim, S. Y. Jeong and C. R. Cho, *J. Power Sources*, 2015, **284**, 392–399.
- 42 G. Z. Fang, J. Zhou, C. W. Liang, A. Q. Pan, C. Zhang, Y. Tang, X. P. Tan, J. Liu and S. Q. Liang, *Nano Energy*, 2016, 26, 57–65.
- 43 B. Yan, L. Chen, Y. J. Liu, G. X. Zhu, C. G. Wang, H. Zhang, G. Yang, H. T. Yec and A. H. Yuan, *CrystEngComm*, 2014, 16, 10227–10234.
- 44 D. Tian, X. L. Zhou, Y. H. Zhang, Z. Zhou and X. H. Bu, *Inorg. Chem.*, 2015, 54, 8159–8161.
- 45 K. Z. Cao, L. F. Jiao, H. Xu, H. Q. Liu, H. Y. Kang, Y. Zhao, Y. C. Liu, Y. J. Wang and H. T. Yuan, *Adv. Sci.*, 2015, 1500185.
- 46 R. B. Wu, X. K. Qian, K. Zhou, J. Wei, J. Lou and P. M. Ajayan, *ACS Nano*, 2014, **8**, 6297–6303.
- 47 W. M. Mei, J. Huang, L. P. Zhu, Z. Z. Ye, Y. Mai and J. P. Tu, *J. Mater. Chem.*, 2012, 22, 9315–9321.
- 48 X. Zhai, W. Yang, M. Li, G. Lv, J. Liu and X. Zhang, *Carbon*, 2013, 65, 277–286.
- 49 S. Xiong, J. S. Chen, X. W. Lou and H. C. Zeng, *Adv. Funct. Mater.*, 2012, 22, 861–871.
- 50 L. Hu, N. Yan, Q. Chen, P. Zhang, H. Zhong, X. Zheng, Y. Li and X. Hu, *Chem. – Eur. J.*, 2012, **18**, 8971–8977.
- 51 A. Ponrouch, P.-L. Taberna, P. Simon and M. R. Palacín, *Electrochim. Acta*, 2012, **61**, 13-18.
- 52 Y. Sun, X. Hu, W. Luo, F. Xia and Y. Huang, *Adv. Funct. Mater.*, 2013, **23**, 2436–2444.
- 53 Y. G. Guo, J. S. Hu and L. J. Wan, Adv. Mater., 2008, 20, 2878–2887.
- 54 D. Tian, X. L. Zhou, Y. H. Zhang, Z. Zhou and X. H. Bu, *Inorg. Chem.*, 2015, 54, 8159–8161.
- 55 S. Li, J. Qiu, C. Lai, M. Ling, H. Zhao and S. Zhang, *Nano Energy*, 2015, **12**, 224–230.
- 56 V. Augustyn, J. Come, M. A. Lowe, J. W. Kim, P. L. Taberna,
 S. H. Tolbert, H. Abrua, P. Simon and B. Dunn, *Nat. Mater.*,
 2013, 12, 518–522.
- 57 H. Lindstrm, S. Sdergren, A. Solbrand, H. Rensmo, J. Hjelm,
 A. Hagfeldt and S. E. Lindquist, *J. Phys. Chem. B*, 1997, 101,
 7717–7722.
- 58 D. F. Xu, C. J. Chen, J. Xie, B. Zhang, L. Miao, J. Cai, Y. H. Huang and L. N. Zhang, *Adv. Energy Mater.*, 2016, 1501929.