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Abstract

A novel hierarchical star-like Co₃O₄ was successfully synthesized from self-assembled hierarchical Co(OH)F precursors via a facile hydrothermal method and subsequent annealing in air. The morphological evolution process of the Co(OH)F precursors was investigated by examining the different reaction times during synthesis. First, hexagonal plates are formed, and then nanodiscs grow on the surface of the plates. Subsequently, dissolution and regrowth of Co(OH)F occur to form the star-like hierarchical structures. Co₃O₄ obtained from thermal decomposition of the Co(OH)F precursor in air at 350 °C exhibited high reversible capacity as an anode material in lithium ion batteries. The specific charge capacity of 1036 mA h g⁻¹ was obtained in the first cycle at a current density of 50 mA g⁻¹, and after 100 cycles, the capacity retention was nearly 100%. When the current density was increased to 500 mA g⁻¹ and 2 A g⁻¹, the capacities were 995 and 641 mA h g⁻¹, respectively, after 100 cycles. In addition, a capacity of 460 mA h g⁻¹ was recorded at a current density of 10 A g⁻¹ in the rate capability test. The excellent electrochemical performance of the Co₃O₄ electrodes can be attributed to the porous interconnected hierarchical nanostructures, which protect the small particles from agglomeration and buffer the volume change during the discharge-charge process.

Keywords

nanostructures, micro, co₃o₄, batteries, ion, like, star, hierarchical, assembly, lithium, self, application, their

Disciplines

Engineering | Science and Technology Studies

Publication Details

Li, L., Seng, K. Hau., Chen, Z., Guo, Z. & Liu, H. Kun. (2013). Self-assembly of hierarchical star-like Co₃O₄ micro/nanostructures and their application in lithium ion batteries. *Nanoscale*, 5 (5), 1922-1928.

Self-assembly of hierarchical star-like Co_3O_4 micro/nanostructures and their application in lithium ion batteries

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Abstract: A novel hierarchical star-like Co_3O_4 was successfully synthesized from self-assembled hierarchical $\text{Co}(\text{OH})\text{F}$ precursors via a facile hydrothermal method and subsequent annealing in air. The morphological evolution process of the $\text{Co}(\text{OH})\text{F}$ precursors was investigated by examining the different reaction times during synthesis. Firstly, hexagonal plates are formed, and then nanodiscs grow on the surface of the plates. Subsequently, dissolution and regrowth of the $\text{Co}(\text{OH})\text{F}$ occur to form the star-like hierarchical structures. The Co_3O_4 obtained from thermal decomposition of the $\text{Co}(\text{OH})\text{F}$ precursor in air at 350 °C exhibited high reversible capacity as anode material in lithium ion batteries. The specific charge capacity of 1036 mAh/g was obtained in the first cycle at the current density of 50 mA/g, and after 100 cycles, the capacity retention was nearly 100%. When the current density was increased to 500 mA/g and 2 A/g, the capacities were 995 and 641 mAh/g, respectively,

after 100 cycles. In addition, a capacity of 460 mAh/g was recorded at current density of 10 A/g in the rate capability test. The excellent electrochemical performance of the Co_3O_4 electrodes can be attributed to the porous interconnected hierarchical nanostructures, which protect the small particles from agglomeration and buffer the volume change during the discharge/charge process.

1. Introduction

Current concerns about limited energy resources and greenhouse gas emissions have brought about the need to consider renewable energies on a larger scale, especially considering the projected widespread use of hybrid and electric vehicles. Lithium ion batteries (LIBs) are currently the dominant power source for all sorts of electronic devices and will be the battery of choice for electric vehicles due to their higher energy density compared to other electrochemical energy storage systems. Nevertheless, the demand for higher energy and higher power LIBs has prompted numerous research efforts toward developing new high-performance electrode materials.¹⁻⁵ In 2000, Tarascon *et al.* proposed transition metal oxides as a new class of negative electrode materials for LIBs, which provide much higher capacity compared to the commercialized graphite (372 mAh/g).^{5(a, b)} This is because transition metal oxides undergo a conversion reaction mechanism where lithium-ions reversibly react with the metal oxides to form Li_2O . Therefore, it is possible to store from 2 to 8 lithium ions per formula unit, depending on the oxidation state of the transition metal.

Cobalt oxide (Co_3O_4) is one of the most promising transition metal oxides, due to its ability to react with up to 8 Li^+ per formula unit, which gives a theoretical capacity of 890 mAh/g. In recent years, many Co_3O_4 nanostructures have been synthesized and studied as anode

materials, in such forms as hollow spheres,^{6(a)} hierarchical sphere,^{6(b)} nanoneedles,⁷ nanowires,⁸ nanocages,⁹ nanotubes,^{10(a)} nanorods,^{10(b)} lemongrass-like^{10(c)} In addition, Co₃O₄/carbon composites such as graphene/Co₃O₄,^{11(a, b)} carbon nanofiber/Co₃O₄,^{12,13(a,b)} and mesoporous carbon/Co₃O₄,^{14(a)} as well as Co(OH)₂/Co₃O₄^{14(b)} were also studied. Although improvements have been made in these reported works in terms of the cycling stability of Co₃O₄, increasing the rate performance (power density) of Co₃O₄ remains a major challenge due to the slow kinetics of the conversion reaction. One generally accepted strategy to increase the rate of the lithium reaction is to decrease the size of individual particles. This will result in an increased active surface area for lithium reaction and also decrease the length of the lithium-ion pathways into the material. Furthermore, anode materials that are microscopically connected to each other could facilitate electron transfer between the current collector and the active materials. Both of these strategies can be accommodated by microstructures with nanosize building blocks, which have been designated as “hierarchical structures” in the literature.

In this study, self-assembled hierarchical microstructures have been successfully prepared via the hydrothermal method to first obtain Co(OH)F precursor, which is then followed by subsequent annealing in air to obtain Co₃O₄. The as-prepared hierarchical Co₃O₄ material displays novel star-like microstructures with a diameter of around 11 μm along every diagonal axis, which are made up of bundled porous nanoneedles. Due to these unique structural features, the material exhibits good cycling stability and rate capability when tested against a lithium metal counter electrode in a half cell. The discharge and charge capacity is stabilized at 1025 and 995 mAh/g, respectively, after 100 cycles at current density of 500 mA/g, so the material demonstrates excellent reversibility. Additionally, in rate capability tests, this

material also showed an average specific charge capacity of 1050, 1040, 976, 736, and 460 mAh/g at the current density of 0.5, 1, 2, 5, and 10 A/g, respectively. To the best of our knowledge, this is the highest rate performance reported so far for Co_3O_4 anodes. The results demonstrate that the self-assembled hierarchical structure can effectively enhance both the cycling stability and the rate performance of Co_3O_4 anode materials for lithium ion batteries.

2. Experimental

Preparation of the $\text{Co}(\text{OH})\text{F}$ precursor: in a typical synthesis, an 0.08 mol/L solution with 0.35 g (1.2 mmol) $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.22 g (6 mmol) NH_4F , and 0.36 g (6 mmol) $\text{CO}(\text{NH}_2)_2$ was dissolved in 15 mL of deionized water under magnetic stirring at room temperature. The as-obtained homogeneous solution was continually stirred for 10 min and then transferred into a Teflon-lined stainless steel autoclave (capacity of 25 mL). The liner was sealed, and the autoclave maintained at 120 °C for 6 h in an electric oven¹⁵. The system was then cooled to ambient temperature naturally. The final pink products were collected and rinsed with deionized water and ethanol three times, followed by drying at 80 °C for 24 h under vacuum. The precursor was then ready for further processing and characterization. To investigate the formation mechanism of the $\text{Co}(\text{OH})\text{F}$, different reaction times (2, 4, and 10 h) were also investigated, and the samples are denoted as Co-2h, Co-4h, Co-6h, and Co-10h.

Preparation of the hierarchical nanostructured Co_3O_4 : the $\text{Co}(\text{OH})\text{F}$ precursors produced with different reaction times were annealed at 350 °C in air for 2 h in a tube furnace, followed by natural cooling to room temperature. The heating rate was set to 5 °C/min.

Material characterization: the structure and morphology of the as-prepared samples were characterized by X-ray diffraction (XRD; MMA GBC, Cu $\text{K}\alpha$ radiation), field emission

scanning electron microscopy (FESEM; JEOL-7500, 2 keV), and transmission electron microscopy (TEM; JEOL-2010, 200 keV).

Electrochemical testing was carried out via CR2032 coin type cells. The working electrodes were prepared by mixing the as-prepared Co₃O₄, carbon black, and poly (vinylidene difluoride) (PVDF) at a weight ratio of 8:1:1. The resultant slurry was pasted on Cu foil and dried in a vacuum oven at 90 °C for 12 h. Coin cells were assembled in an argon-filled glove box (Mbraun, Unilab, Germany) by stacking a porous polypropylene separator containing liquid electrolyte between the composite electrode and a lithium foil counter electrode. The electrolyte consisted of a solution of 1 M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1:1, v/v). Cyclic voltammograms were collected on a VMP-3 electrochemical workstation at a scan rate of 0.1 mV/s. The discharge and charge measurements were conducted on a Land CT2001A battery tester.

3. Results and discussion

A typical XRD pattern of the as-prepared star-like Co(OH)F (Co-6h) is presented in Fig. 1. All of the diffraction peaks can be ascribed to the Co(OH)F phase with an orthorhombic structure (PDF#50-0827, $a = 10.28864 \text{ \AA}$, $b = 4.68307 \text{ \AA}$, and $c = 3.13011 \text{ \AA}$). In addition, no diffraction peaks corresponding to Co(OH)₂ can be detected, signifying that the as-prepared material is Co(OH)F. The formation of Co(OH)F can be described by the following steps:

It should be mentioned that the urea used in the present synthesis mainly serves as a source for the generation of hydroxyl anions, as explained in Equation (1), while the divalent cobalt cations and fluoride anions required in Equation (3) are from $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and NH_4F .

Fig. 1 X-ray diffraction pattern of the as-prepared $\text{Co}(\text{OH})\text{F}$ (Co-6h) precursor

The morphology of the as-prepared $\text{Co}(\text{OH})\text{F}$ (Co-6h) was investigated using field-emission scanning electron microscopy (FE-SEM), and a panoramic view of this solid sample (Fig. 2(a)) reveals uniform star-like structures, assembled from bundles of nanoneedles with lengths of 12-15 micrometers along every diagonal axis (Fig. 2(b)). The long nanoneedles of this star-like assembly share a common centre and extrude outwards along the radial direction (Fig. 2(c)). The detailed structure and the growth direction of the $\text{Co}(\text{OH})\text{F}$ nanoneedles were further examined by transmission electron microscopy (TEM). Fig. 2(d) shows a TEM image of a single nanoneedle with a very smooth surface and a diameter of approximately 50 nm. The high resolution TEM (HR-TEM) image in Fig. 2(e) is the corresponding image of the area marked by the red circle in Fig. 2(d). It shows an interplanar distance of 0.42 nm, matching the

d-spacing of the (110) crystal planes of orthorhombic Co(OH)F. In addition, Fig. 2(f) shows the corresponding electron diffraction pattern, which reveals diffraction spots indicating the single-crystalline nature of the nanoneedles and their preferential growth along the [111] direction.

Fig.2 FE-SEM images at different magnifications (a, b, c) of the hierarchical star-like Co(OH)F (Co-6h) micro/nanostructures assembled from nanoneedle bundles. (d) TEM image of an individual nanoneedle of Co(OH)F (Co-6h). (e) HR-TEM image of the area marked with the red circle in (d). (f) The corresponding selected area electron diffraction pattern of Co(OH)F (Co-6h).

In order to understand the evolution process of the star-like Co(OH)F , a series of time-dependent experiments were conducted. Fig. S1 (Supplementary Information) displays a series of XRD patterns of the Co(OH)F samples obtained at different reaction times. The characteristic peaks of the products obtained at the reaction times of 2 h and 4 h were in good agreement with those for the sample with the reaction time of 6 h, which can be indexed to orthorhombic Co(OH)F . After increasing the reaction time to 10 h, however, some impure peaks appeared in the XRD pattern which can be indexed to $\text{Co(OH)}_{0.7}\text{F}_{1.3}$. The morphologies

of these intermediate products at the different reaction stages were also examined. Fig. 3(a-f) shows representative SEM images of the samples, which were collected stepwise after 2, 4, and 10 h of reaction, and a schematic representation of the morphological evolution process of the star-like Co(OH)F is presented in Fig. 3(g). After 2 hours of reaction time (Co-2h), hexagonal microplates were formed with diameters ranging from 2 to 5 μm and thickness of less than 1 μm (Fig. 3(a, b)). The products from 4 hours of reaction time (Co-4h) look similar to those from 2 hours (Co-2h) at first glance. Upon closer inspection, however, nanodiscs were found to be growing on the surface of the microplates (Fig. 3(d)). Furthermore, partially formed star-like structures were also found; however, the nanoneedles were not well developed, as shown in the inset of Fig. 3(c). After 6 hours of reaction time, the majority of the products were star-like hierarchical structures, as shown in Fig. 2(a). When the reaction time was extended to 10 h, the star-like structures turned into flower-like hexagonal plate structures. The surfaces of these hexagonal plates show semicircular shaped petals resembling those of a flower (Fig. 3(f, g)). The formation of the hexagonal plates with compact surfaces may be due to the minimization of surface energy and subsequent Ostwald ripening, in which the nanoneedles dissolve and regrow into the compact hexagonal plates. A similar phenomenon has been reported by Cao *et al.* on the formation of hexagonal cobalt plates.¹⁶ Besides, the formations of the hexagonal plates were also studied at reaction times of 10, 30 and 60 minutes. We found that there were no precipitates when the reaction times were 10 and 30 minutes, and the solution remained bright pink indicating little or no reaction occurring. As the reaction time was increased to 60 minutes, pink precipitates of less than 20 mg were collected. The sample reacted for 60 minutes (Co-1h) was investigated using SEM, and the images are shown in Fig. S2 (Supplementary Information). The morphology of Co-1h is very similar to Co-2h, where

hexagonal microplates with diameter ranging from 3 to 4 micrometers and thickness of less than 1 micrometer were observed.

In order to prepare Co_3O_4 star-like structures (Co-6h-A), we annealed the Co-6h sample in air at 350 °C for 2 hours. Fig. 4 shows the XRD pattern of the Co_3O_4 sample after annealing, and the peaks in the XRD pattern can be indexed as crystalline Co_3O_4 (PDF# 43-1003, cubic symmetry, space group $Fd3m$, lattice constant $a = 8.09011 \text{ \AA}$). No other peaks were found, and the Co(OH)F is thus fully converted to Co_3O_4 . The morphological and structural characterizations of the Co-6h-A were carried out using both FE-SEM and TEM (HR-TEM). Typical low magnification FE-SEM images of the star-like Co_3O_4 are shown in Fig. 5(a, b). Note that the diagonal axes are around 12-15 μm in length, which are very similar in size to those of its precursor (Fig. 2(b)). Although the Co-6h-A sample still preserves the star-like microstructure, the surface of the sample looks very rough, as shown in Fig. 5(c). This is due to the associated gas release and dehydration of the precursor during the annealing of Co(OH)F precursor, which leads to the end product, Co_3O_4 , forming a porous structure. The sample was further characterized using TEM, and the image of an individual nanoneedle is shown in Fig. 5(d). The morphology of the nanoneedles agrees with that observed from SEM. The nanoneedles became porous, and they are clearly made from interconnected particles of Co_3O_4 . The grain size of the individual Co_3O_4 nanocrystals shown in Fig. 5(e) is in the range of 15-20 nm, and the pore size is about 5 nm. An HR-TEM image of Co_3O_4 nanocrystals with lattice fringes is shown in Fig. 5(f1), and the corresponding fast Fourier transform – electron diffraction (FFT-ED) pattern is shown in Fig. 5(f2). The interplanar spacings are measured to be 0.47 nm and 0.28 nm,

Fig. 3 FE-SEM images of Co(OH)F precursors obtained at different reaction times: (a, b) 2 h; (c, d) 4 h, (inset is the high resolution image of the area marked by the red circle in Fig. (c)); (e, f) 10 h; (g) schematic representation of the evolution of the Co(OH)F precursor with the reaction time.

corresponding to the (111) and (002) crystal planes of Co_3O_4 . It is noteworthy that pores around 4 nm in diameter exist between the interconnected nanocrystalline Co_3O_4 grains (15-20 nm), which can promote soaking of the electrolyte into the material, thus shortening the intercalation pathways of Li^+ ions as they move into the Co_3O_4 host structure, therefore enhancing its electrochemical performance as anode material for LIBs. In addition, the samples at different heating temperature (400 °C and 450 °C) were also conducted, and the FE-SEM images are shown in Fig.S3 (Supplementary Information).

To further investigate the specific surface areas and the porous nature of the Co_3O_4 (Co-6h-A), the N_2 adsorption-desorption isotherm at 77 K was reported in Fig.

S4(Supplementary Information), with the inset showing their corresponding Barrett–Joyner–Halenda (BJH) pore-size distribution. The BET specific surface area is 25 m²/g. The BJH pore-size-distribution curve (inset) indicates that majority of the pores are around 2.2 nm in diameter, and there are also pores ranging from 5 to 100 nm present in the sample.

Furthermore, the star-like Co₃O₄ (Co-6h-A) was tested for its lithium storage properties as an anode material for LIBs in a coin-type half-cell against lithium metal counter electrode. The galvanostatic discharge/charge profiles of the Co₃O₄ electrode at

Fig. 4 X-ray diffraction pattern of the star-like Co₃O₄ (Co-6h).

a current density of 50 mA/g are displayed in Fig. 6(a). In the first discharge, a short plateau at 1.25 V and a longer plateau at 1.1 V can be observed, which can be ascribed to the reduction process to CoO and metallic Co, as well as the formation of amorphous Li₂O ($\text{Co}_3\text{O}_4 + 8\text{Li}^+ + 8\text{e}^- = 3\text{Co} + 4\text{Li}_2\text{O}$). For the first charge, a voltage plateau at around 2.4 V is recorded, corresponding to the process of oxidation of metallic Co to Co₃O₄ and the decomposition of the Li₂O matrix.

In addition, cyclic voltammetry (CV) was also performed on the Co-6h-A sample, and the results are plotted in Fig. S5 (Supplementary Information). The CV shows peaks that correspond to the voltage profile, thus confirming the electrochemical reaction in the material.

Furthermore, the discharge/charge profiles are consistent with those of other transition metal oxides, such as Fe and Ni oxides, which involve the formation and decomposition of Li_2O and accompanying reduction and oxidation of metal nanoparticles, as reported by P. Poizot et al.¹⁷

The initial discharge capacity of the star-like Co_3O_4 (Co-6h-A) electrode is 1324 mAh/g (~11.9 mol of Li),¹⁸ while the initial charge capacity is 1036 mAh/g (~ 9.3 mol of Li), accounting for an initial coulombic efficiency of 78%. The irreversible capacity during the first cycle can be attributed to the formation of the solid electrolyte interphase (SEI) layer.^{10(a), 11(a)} It is noteworthy that the discharge and charge capacities recorded were higher than the theoretical capacity of 890 mAh/g for the 8 Li^+ reaction with Co_3O_4 . The extra capacity recorded can be explained by two mechanisms which were previously reported,¹⁸ namely, electrolyte decomposition^{19,20} and interfacial storage.²¹

Fig. 5 FE-SEM images at different magnifications (a, b, c) of the star-like Co_3O_4 nanoneedle arrays. (d) TEM image of an individual nanoneedle of Co_3O_4 , and (e) high resolution image of Co_3O_4 nanoneedle. (f1) HR-TEM image of lattice fringes of Co_3O_4 nanoneedle. (f2)

Corresponding FFT-ED pattern generated from Fig. 5(f1). (f3) Growth direction of Co_3O_4 in the selected area in (f1). (f4) Corresponding inverse FFT (IFFT)-ED pattern generated from Fig. 5(f2).e former would lead to the formation of a gel-like polymeric layer on the surface of the active material particles, which possibly contributes to the preservation of the active material's integrity. In addition, it is also believed to enable additional lithium storage on its surface in a capacitive way, therefore contributing to the observed extra capacity. The second mechanism is based on a two-phase capacitive behaviour of the $\text{Li}_2\text{O}/\text{Co}$ interface that allows for the storage of Li^+ ions on the lithium compound side, whereas electrons are localized on the metallic side, thus leading to a charge separation²² and extra capacity at low voltage.

The cycling performance of the star-like Co_3O_4 (Co-6h-A) electrode at different current densities is shown in Fig. 6(b). It should be noted that the reversible discharge/charge capacity gradually increases to 1300 mAh/g and 1278 mAh/g, respectively, over the first 25 cycles at the current density of 50 mA/g, and the reason for the increasing capacity should agree with the two mechanisms discussed above. Then, the capacity gradually decreases to 1200 mAh/g at the 60th cycle and remains stable up to the 100th cycle. We can observe that the capacity after 100 cycles was still higher than that of the theoretical capacity, and the reason is likely due to the reversible formation and decomposition of gel-like polymeric layer on the surface of the active material during the charge/discharge process. A similar trend can also be observed when the current densities are set to 0.5 A/g and 2 A/g (Fig. 6(b)). The specific discharge and charge capacities recorded were 1025 and 995 mAh/g, respectively, after the 100th cycle at 0.5 A/g, while 660 and 641 mAh/g were recorded, respectively, after 100 cycles at the current density of 2 A/g, which demonstrates the excellent cycling stability of star-like Co_3O_4 as anode material, even at high current densities.

The rate capability was also investigated, and the results are presented in Fig. 6(c). The

discharge current density was fixed at 0.5 A/g, while the charge current density was varied at 0.5, 1, 2, 5, and 10 A/g. The average charge capacity of 1050, 1040, 976, 736, and 460 mAh/g were recorded at 0.5, 1, 2, 5, and 10 A/g, respectively. It should be noted that in the first 20 cycles, when the current density increased from 0.5 A/g to 1 A/g, the specific capacity of the star-like Co_3O_4 electrode still increased gradually, which is in good agreement with the results from the cycling performance, as shown in Fig. 6(b). Furthermore, the charge specific capacity obtained at 10 A/g is 43.8 % of the capacity obtained at the current density of 0.5 A/g and is still higher than the theoretical capacity (372 mAh/g) of graphite. More importantly, when the current density was decreased back to 0.5 A/g again after 50 cycles, an average specific charge capacity of 1140 mAh/g was recovered, which is slightly higher than the initial charge capacity at the current density of 0.5 A/g, indicating the high cycling stability of star-like Co_3O_4 as anode material for LIBs and further confirming the results from Fig. 6(b).

In order to compare the lithium storage performance of our star-like Co_3O_4 sample with previously published reports on Co_3O_4 nanostructures, we have listed the electrochemical performances in Table S1 (Supplementary Information) for comparison. From Table S1, we can see that the star-like Co_3O_4 in this work exhibits the highest initial capacity, the highest coulombic efficiency, and the highest capacity after cycling, compared to those reported Co_3O_4 samples in the forms of hollow spheres,^{6(a)} needles,⁷ nanowires,⁸ nanocages,⁹ and nanotubes^{10(a)}, as well as in graphene or carbon/ Co_3O_4 composites.^{11(a),12,14(a)}

As it combines highly reversible capacity, excellent cycling stability, and high coulombic efficiency with good rate capability, we believe that star-like Co_3O_4 with porous nanoneedle bundles is a good candidate as anode material for the LIB. The superior electrochemical performance of this star-like Co_3O_4 electrode can probably be attributed to the nanometer-sized subunits and pores. The small interconnected Co_3O_4 nanoparticles provide a fast and efficient transport pathway for Li ions. The porous structure of the nanoneedles contributes to the high

specific surface area, making the electrochemical reaction with lithium more active,⁸ and the internal pores allow the Co_3O_4 to effectively buffer the volume change during the discharge/charge process; therefore, it can maintain the integrity of the electrodes during cycling and also maintain the cycling stability of the electrodes.

Fig. 6 (a) Galvanostatic charge/discharge profiles of Co_3O_4 (Co-6h) for selected cycles at the current density of 50 mA/g, with the potential window from 0.01 V to 3 V; (b) cycling

performance of Co_3O_4 (Co-6h) at the charge/discharge current densities of 50 mA/g, 500 mA/g, and 2 A/g; (c) rate performance of Co_3O_4 (Co-6h) electrode; the discharge current density is fixed at 0.5 A/g.

4. Conclusions

In summary, we implemented a hydrothermal route to prepare $\text{Co}(\text{OH})\text{F}$ hierarchical micro/nanostructures that are assembled from smaller building units of single-crystalline nanoneedles. The effects of the hydrothermal reaction time on the morphology of the precursors have been investigated in detail. With this synthetic route, the precursor $\text{Co}(\text{OH})\text{F}$ compound was actually obtained through a gradual morphological evolution from single hexagonal microplates, to nanodiscs assembled on microplates, to hierarchical nanoneedles assembled on star-like microplates, and finally to the flower-like circular microplates. Using this solid precursor, we have also successfully prepared star-like Co_3O_4 nanoneedle arrays via direct thermal decomposition in air at 350 °C. As the anode material for lithium ion batteries, the star-like Co_3O_4 electrode exhibited highly reversible capacity, with specific charge capacity of 1036 mAh/g in the first cycle at the current density of 50 mA/g, and by 100 cycles, the retained capacity was nearly 100 %. On increasing the current density to 500 mA/g and 2 A/g, the capacities were 995 and 641 mAh/g after 100 cycles. In addition, a capacity of 460 mAh/g could still be obtained at the even higher current density of 10 A/g. The excellent electrochemical performance of the Co_3O_4 electrodes is proposed to be due to the porous interconnected hierarchical nanostructures, which prevent the small particles from agglomerating and buffer the volume change during the discharge/charge process.

Acknowledgements

This work was funded by an Australian Research Council (ARC) Discovery Project

(DP1094261), The authors also would like to thank Dr. Tania Silver at the University of Wollongong for critical reading of the manuscript and Mr. Darren Attard for his great contribution.

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Electronic Supplementary Information

Fig. S1 XRD patterns of Co(OH)F precursors obtained at different reaction times: (a) 2 h, (b) 4 h, (c) 10 h.

Fig S2. FE-SEM images of Co(OH)F precursor obtained at reaction time of 60 min

Fig.S3 FE-SEM images of Co_3O_4 (Co-6-A) annealed at 400°C and 450°C, respectively

We have treated the star-like $\text{Co}(\text{OH})\text{F}$ precursor to 400 °C and 450 °C. Fig. S3(a-c) show the images of the sample annealed at 400 °C and Fig. S3(d-f) show the images of the sample annealed at 450°C. The star-like structure was partially destroyed when the sample was annealed to 400 °C. In addition, the individual particle size became larger (up to 100 nm; Fig. S3(c)) compared to the particle size which is less than 20 nm when annealed at 350 °C (Fig. 5(c, d)). When the annealing temperature was increased to 450 °C, no star-like structures were observed. This is most likely due to the higher annealing temperature which shattered the structure. However, some bundled structures remained and the individual particle sizes have also increased to more than 100 nm.

As the star-like structures were not preserved after annealing at temperatures of 400 °C and 450 °C, we did not proceed to test the electrochemical performances.

Fig.S4 Nitrogen adsorption-desorption isotherm and pore-size-distribution curve (inset) of Co_3O_4 (Co-6-A).

Fig. S5 CV curves for the first 5 cycles of the Co-6h-A electrode with 0.1 mV/s scan rate in the potential window from 0.01 to 3 V.

Fig. S6 FE-SEM images (a and b) and TEM images (c and d) of the star-like Co_3O_4 electrode after 100 cycles.

The SEM and TEM images of the star-like Co_3O_4 after 100 cycles are presented in Fig. S6. It can be noted from the SEM images that the integrity of the electrode remains even after 100 charge/discharge cycles. The star-like structures were no longer observed, and this may be due to several reasons such as: (1) being covered by the carbon additive, PVDF binder and SEI layer; (2) electrochemical milling effect; (3) volume and phase changes during cycling. The latter two is very common for transition metal oxide anode which undergoes conversion reaction. Although the star-like microstructures were no longer observed, the nano-needles were partially preserved, as observed from the TEM images. We could not obtain a high resolution TEM image of due to the interference of the unstable SEI layer around the nano-needles which deforms under focused electron beam.

Table S1 Comparison of electrochemical performance of Co₃O₄ as anode material for the LIB,
as reported in the recent literature.

Materials	Current density (mA/g)	Initial charge specific capacity (mAh/g)	Initial coulombic efficiency	Charge capacity after cycling (mAh/g)
Hollow sphere Co ₃ O ₄ ⁶	178	1131	74%	866 after 50 cycles
needle-like Co ₃ O ₄ ⁷	50	950	58.7%	<500 after 80 cycles
Co ₃ O ₄ nanowires ⁸	111	859	76.4%	700 after 20 cycles
Co ₃ O ₄ nanocages ⁹	50	741	73.56%	970 after 30 cycles
Co ₃ O ₄ nanotubes ^{10(a)}	50	850	-	500 after 100 cycles
carbon nanofiber/Co ₃ O ₄ ¹²	100	946.8	77%	776.3 after 100 cycles
mesoporous carbon/Co ₃ O ₄ ^{14(a)}	70	703	33%	541 after 30 cycles
graphene/Co ₃ O ₄ nanoparticles ^{11(a)}	50	753	68.6%	935 after 30 cycles
This work hierarchical star-like Co ₃ O ₄	50	1036	78%	1200 after 100 cycles
	500	984		995 after 100