Electronic Supplementary Information

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

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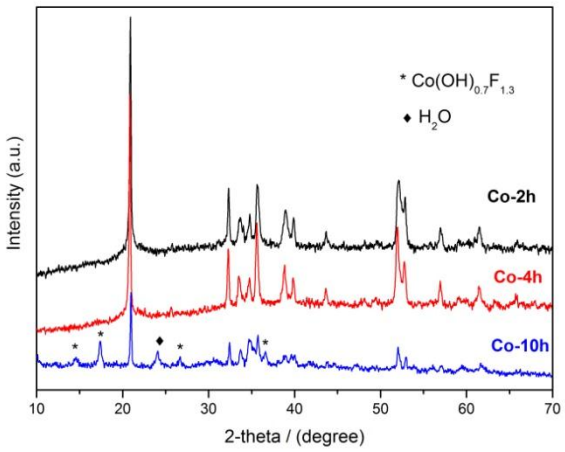


Fig. S1 XRD patterns of Co(OH)F precursors obtained at different reaction times: (a) 2 h, (b) 4 h, (c) 10 h.

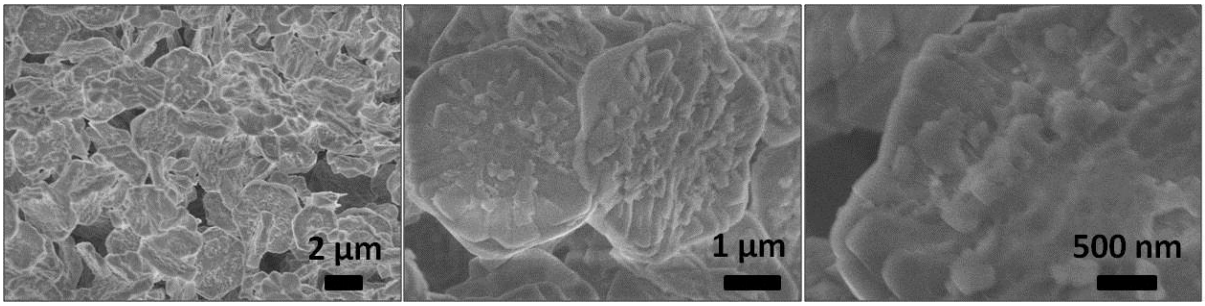


Fig S2. FE-SEM images of Co(OH)F precursor obtained at reaction time of 60 min

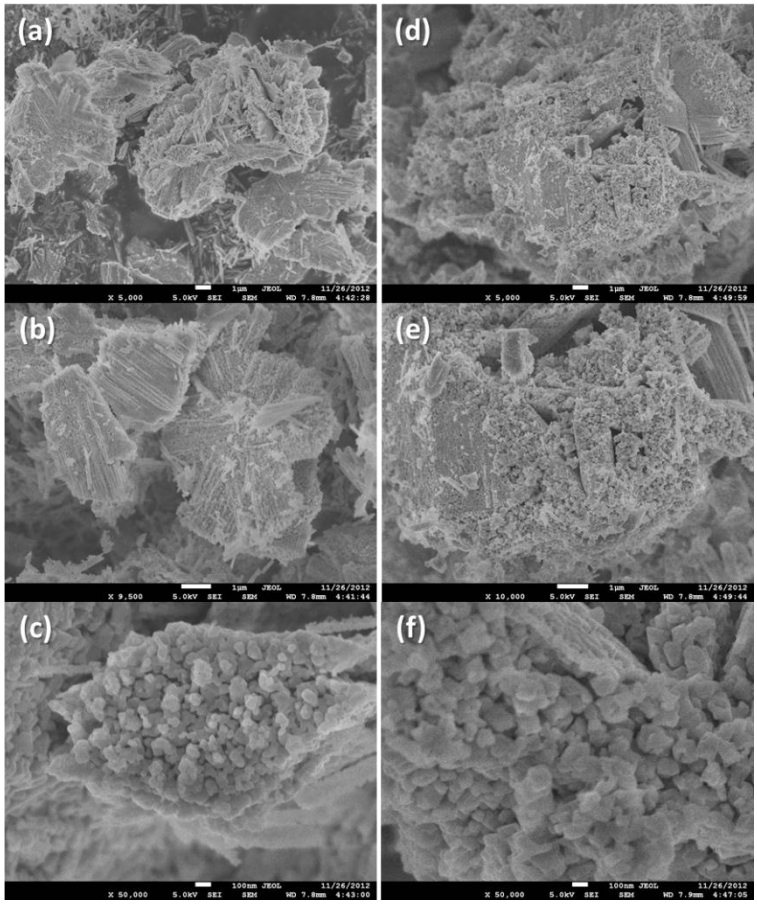


Fig.S3 FE-SEM images of $Co_3O_4$ (Co-6-A) annealed at 400°C and 450°C, respectively

We have treated the star-like Co(OH)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.

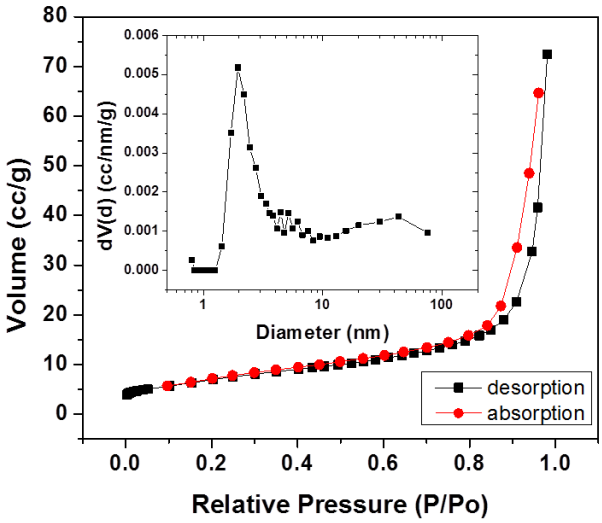


Fig.S4 Nitrogen adsorption-desorption isotherm and pore-size-distribution curve (inset) of $Co_3O_4$ (Co-6-A).

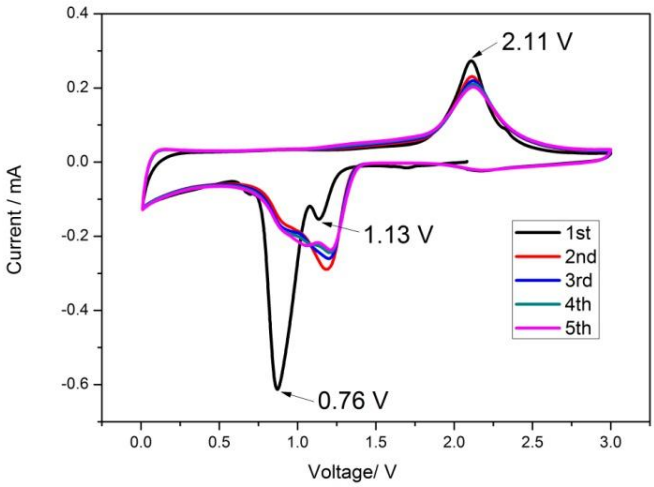


Fig. S5 CV curves for the first 5 cycles of the Co-6h-A electrode with 0.1 mV/s scan rate in the potential window from 0.01 to 3 V.

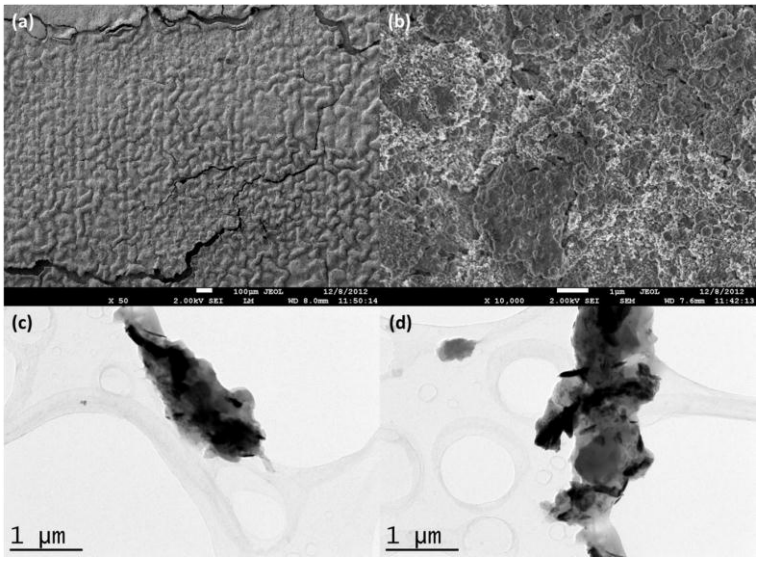


Fig. S6 FE-SEM images (a and b) and TEM images (c and d) of the star-like $Co_3O_4$ electrode after 100 cycles.

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 $Co_3O_4$ 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 $Co_3O_4$ [6] | 178 | 1131 | 74% | 866 after 50 cycles |
| needle-like $Co_3O_4$ [7] | 50 | 950 | 58.7% | <500 after 80 cycles |
| $Co_3O_4$ nanowires [8] | 111 | 859 | 76.4% | 700 after 20 cycles |
| $Co_3O_4$ nanocages [9] | 50 | 741 | 73.56% | 970 after 30 cycles |
| $Co_3O_4$ nanotubes [10(a)] | 50 | 850 | - | 500 after 100 cycles |
| carbon nanofiber/$Co_3O_4$ [12] | 100 | 946.8 | 77% | 776.3 after 100 cycles |
| mesoporous carbon/$Co_3O_4$ [14(a)] | 70 | 703 | 33% | 541 after 30 cycles |
| graphene /$Co_3O_4$ nanoparticles [11(a)] | 50 | 753 | 68.6% | 935 after 30 cycles |
| This work | 50 | 1036 | 78% | 1200 after 100 cycles |
| hierarchical star-like $Co_3O_4$ | 500 | 984 | | 995 after 100 cycles |
| | 2000 | 730 | | 641 after 100 cycles |