Supplementary Information for "An Oil Droplet Template Method for the Synthesis of Hierarchical Structured Co_3O_4/C Anodes for Li-ion Batteries" by

Jie Sun, Haimei Liu, Xu Chen, David G. Evans, Wensheng Yang*

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, Beijing 100029, PR China

As shown in Fig. S1, the LDH superposed nanoplates with different number of shells can be synthesized via changing the amount of LDH nanosheets by adjusting the concentration of cobalt ions in the aqueous phase.

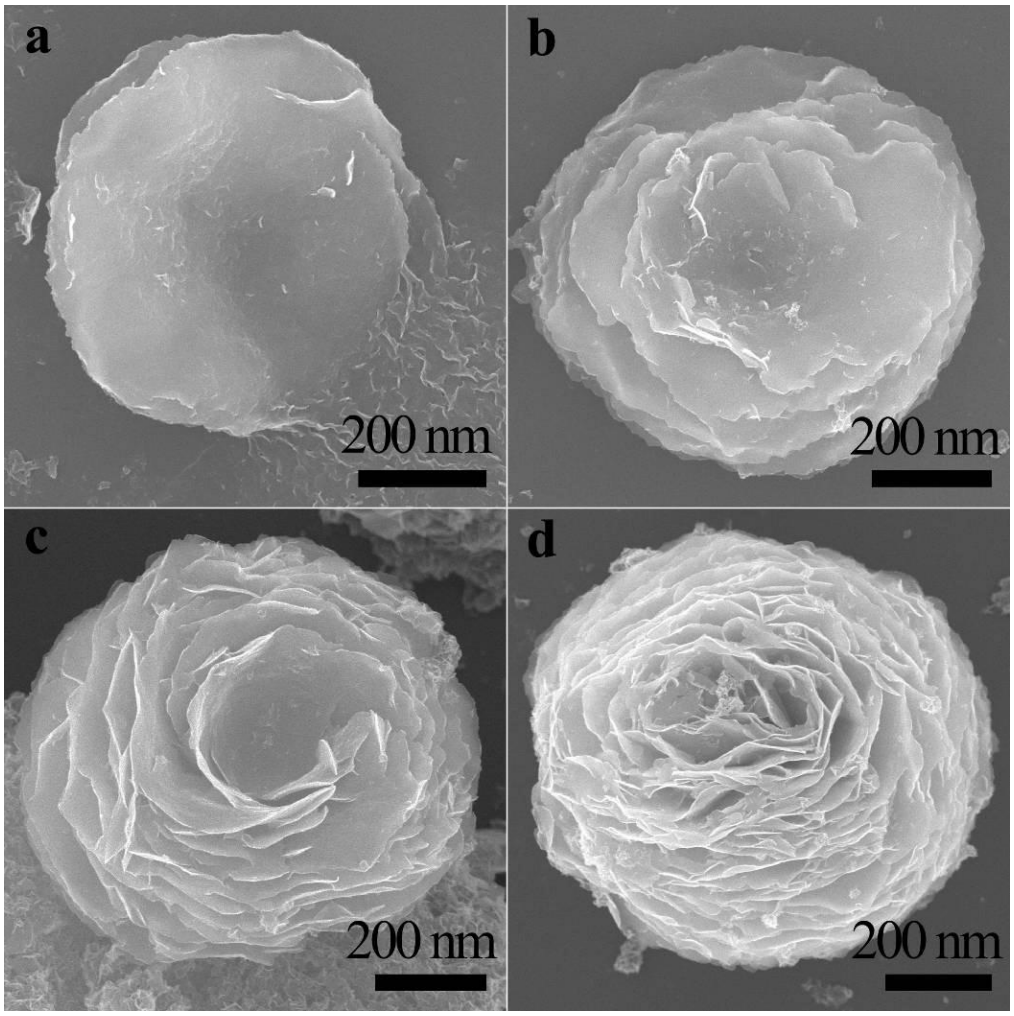

Fig. S1 SEM images of superposed LDH nanoplates with different numbers of layers, which were obtained by changing the amount of $Co(NO_3)_2 \cdot 6H_2O$ and hydrogen peroxide solution (30%) added to the aqueous phase: (a) 0.003 mol $Co(NO_3)_2 \cdot 6H_2O$ and 0.076 mL hydrogen peroxide solution; (b) 0.015 mol $Co(NO_3)_2 \cdot 6H_2O$ and 0.38 mL hydrogen peroxide solution; (c) 0.04 mol $Co(NO_3)_2 \cdot 6H_2O$ and 1.02 mL hydrogen peroxide solution; (d) 0.08 mol $Co(NO_3)_2 \cdot 6H_2O$ and 2.04 mL hydrogen peroxide solution. The other experimental conditions the same as those described in Experimental part in main article.

The FTIR spectrum of the Co_3O_4/C is shown in Fig. S2. The distinct peaks at 663.5 cm^{-1} and 569.4 cm^{-1} are assigned to the ν(Co–O)modes,which confirm the formation of Co_3O_4.[1] The peaks at 2930 cm^{-1} and 2850 cm^{-1} are assigned to CH_2 groups of surfactant-derived amorphous carbon. The broad bands at 3420 cm^{-1} and 1626 cm^{-1} are assigned to OH stretching and bending modes of physically absorbed water, respectively.[1]

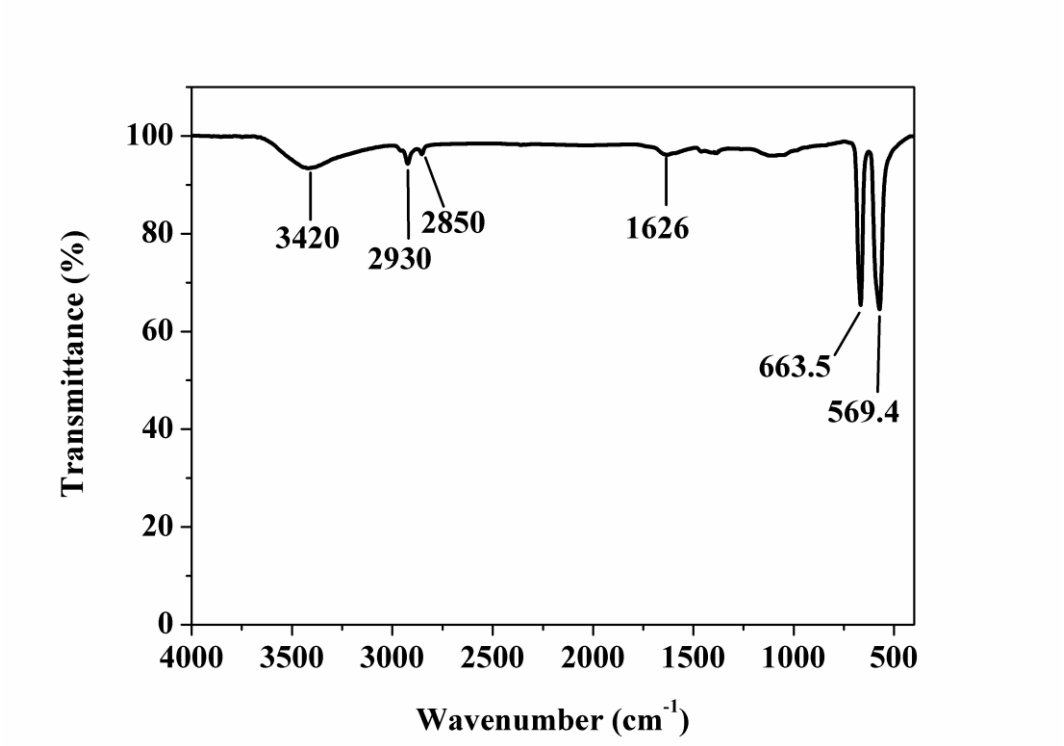

Fig. S2 FT-IR spectrum of the superposed Co_3O_4/C nanoplates.

Fig. S3a shows the regional Co2*p* spectrum of the Co_3O_4/C. The Co2*p* spectrum show a doublet containing a low energy band (Co2$p_{3/2}$) and a high energy band (Co2$p_{1/2}$) at 780.4 and 795.6 eV. The energy difference between the peak of Co2$p_{3/2}$ and Co2$p_{1/2}$ splitting is approximately 15 eV, which indicates the presence of both Co^{2+}/Co^{3+} species in Co_3O_4/C.[2] It can be observed that weak 2*p* satellite features are found at binding energies of 788.9 and 804.3 eV for the prepared cobalt oxides. It has been reported that the weak satellite structures are characteristic of spinels tructures in which 3+ cations occupy octahedral lattice sites with diamagnetic, filled t_{2g} and empty e_g levels, and 2+ cations are in tetrahedral sites.[2] As shown in C1*s* spectrum (Fig. S3b), the peak at 284.6 eV correspond to the C−C bonding from surfactant-derived amorphous carbon.

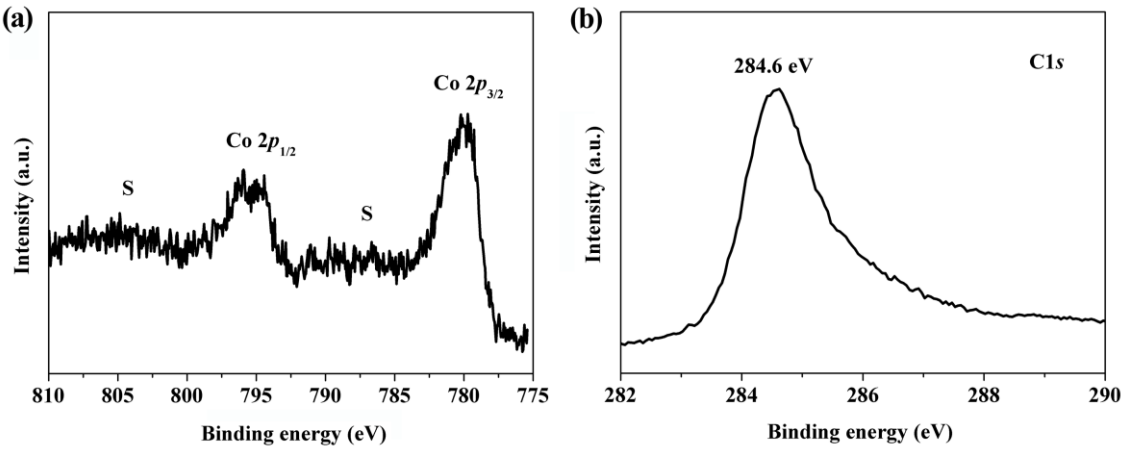

Fig. S3 XPS spectra of the superposed Co_3O_4/C nanoplates: (a) Co2*p* and (b) C1*s*.

As shown in Fig. S4 (a), (c) and (e), the Co_3O_4/C electrode maintained the binder-free film integrity during the 30 cycles. At the discharged state for the first cycle (Fig. S4b), the void space between the shells can correctly accommodate the volume after expansion. At the recharged state for the first cycle (Fig. S4d), the volumetric contraction made some holes in each of the shell. After 30 cylces, the shape integrity can be maintained, as can be seen in Fig. S4f.

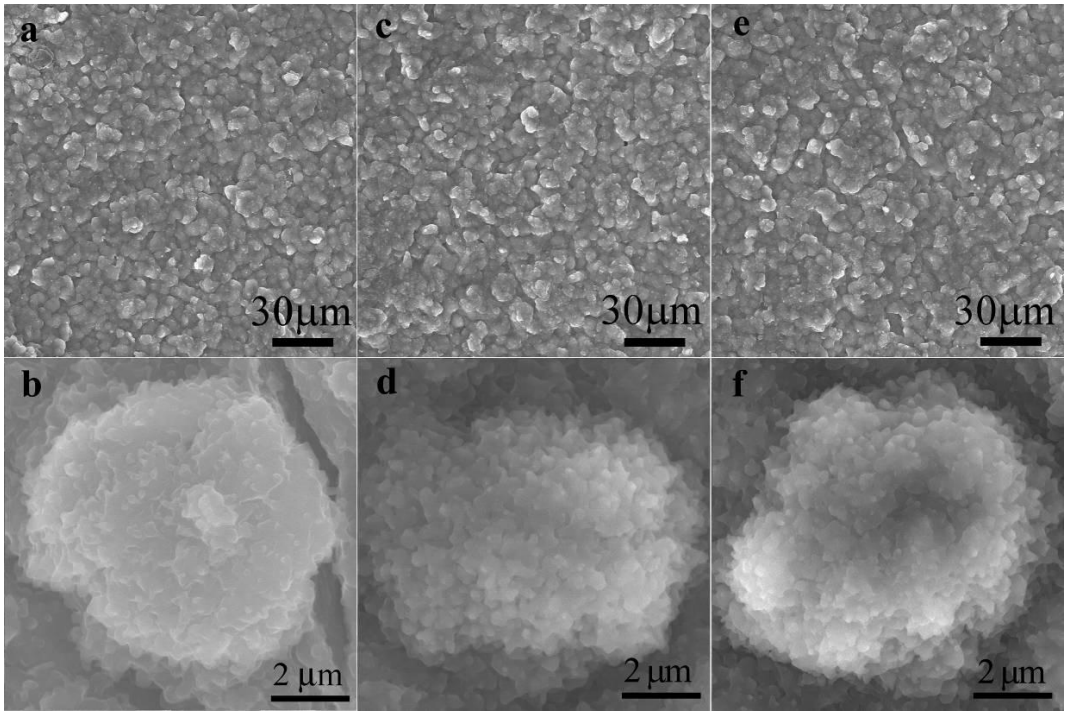

Fig. S4 SEM images of Co_3O_4/C electrode at different states: (a) and (b) the discharged state for the first cycle; (c) and (d) the charged state for the first cycle; (e) and (f) the charged state for the 30th cycle.

Reference

[1] S. M. Agawane and J. M. Nagarkar, *Catal.Sci.Technol.*, 2012, **2**, 1324–1327.

[2] J. Xu, P. Gao and T.S. Zhao, *Energy Environ. Sci.*, 2012, **5**, 5333–5339.