

Supporting Information

Fabrication of hierarchical mesoporous MnCo_2O_4 and CoMn_2O_4 microspheres that are composed of polyhedral nanoparticles as promising anodes for long-life LIBs

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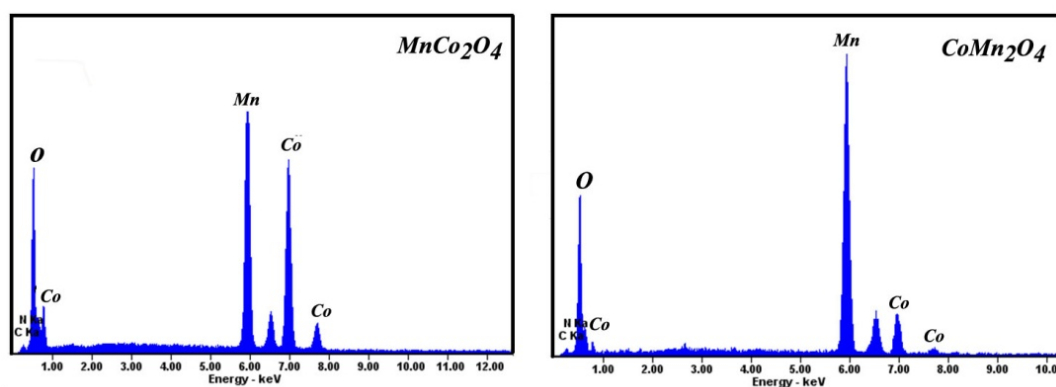


Fig. S1 EDX spectra of the as-obtained MnCo_2O_4 and CoMn_2O_4 .

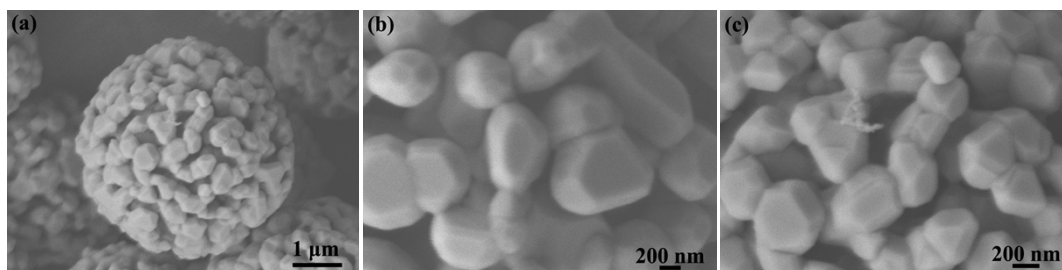


Fig. S2 Magnified SEM images of the porous MnCo_2O_4 microsphere.

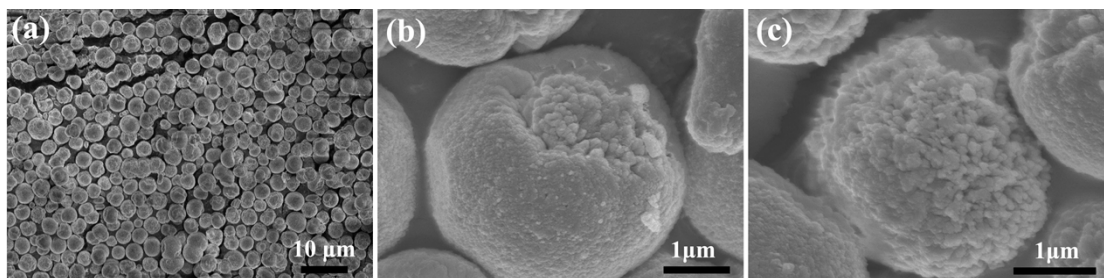


Fig. S3 FESEM images of $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ (MnCo-precursor).

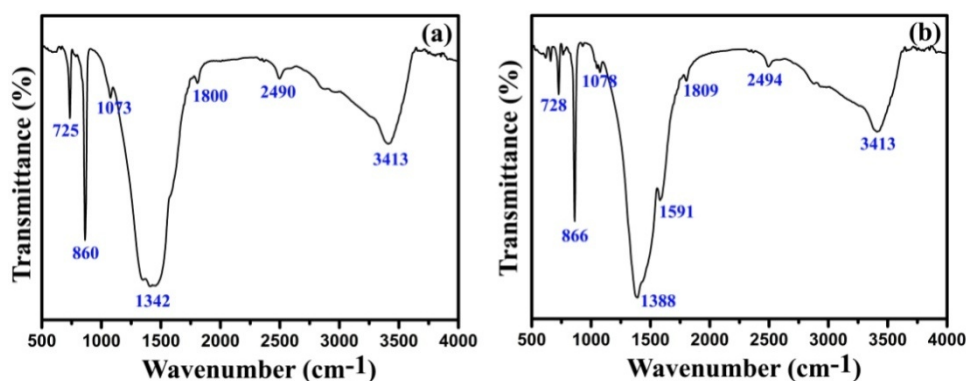


Fig. S4 FTIR spectra of the precursors of (a) $\text{Mn}_{0.33}\text{Co}_{0.67}$ and (b) $\text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3$.

The peak centered at 3413cm^{-1} evidences the presence of O-H stretching vibration, indicating a tiny amount of moisture exists in samples. The stretching vibration and the in-plane flexural vibration of the N-H bond are observed at 2490 and 1800cm^{-1} , respectively, which come from HMT adsorption on the precursors. In addition, the peaks at 1388 , 1073 , 866 , 728cm^{-1} , a feature of carbonate,^[1-2] can be ascribed to the $\text{Mn}_{0.33}\text{Co}_{0.67}$ and $\text{Co}_{0.33}\text{Mn}_{0.67}\text{CO}_3$ precursors.

[1] P. Huang, X. Zhang, J. M. Wei, J. Q. Pan, Y. Z. Sheng, B. X. Feng, *Mater. Chem. Phys.*, **2014**, *147*, 996.

[2] L. M. Song, S. J. Zhang, X. Q. Wu, Z. L. Wang, Q. W. Wei, *Chem. Eng. J.*, **2012**, *15*, 195.

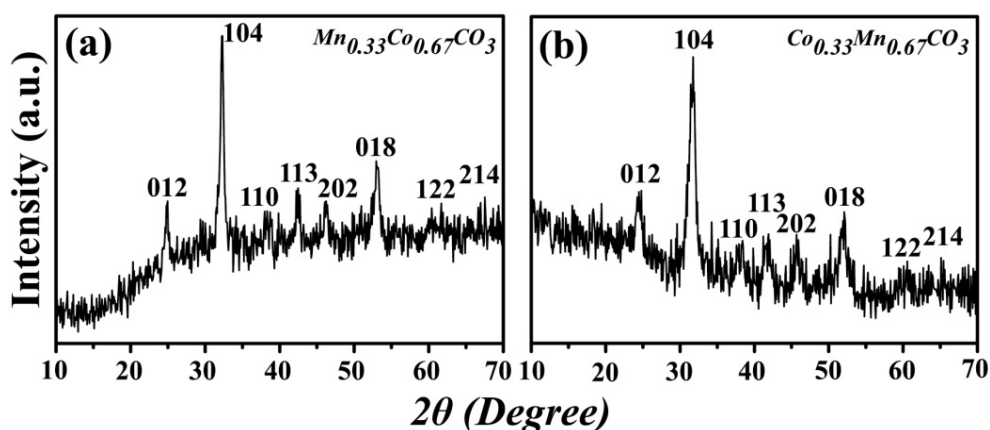


Fig. S5 XRD patterns of the precursors of (a) $Mn_{0.33}Co_{0.67}CO_3$ and (b) $Co_{0.33}Mn_{0.67}CO_3$.

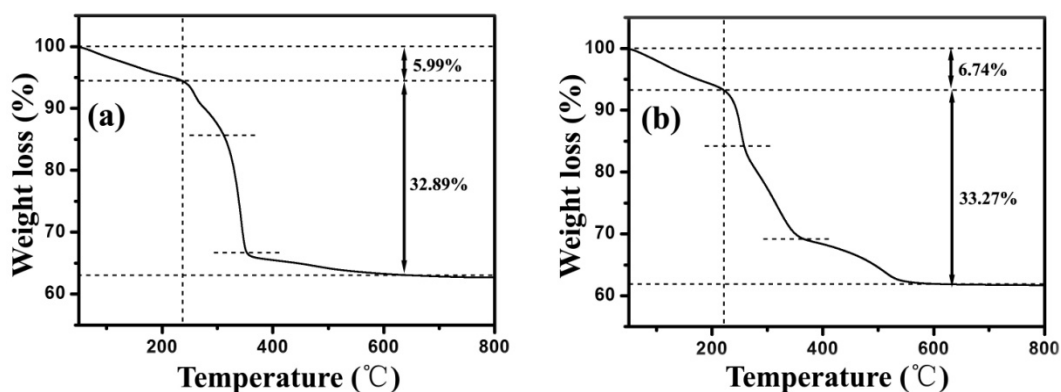


Fig. S6 TGA curves of the (a) $Mn_{0.33}Co_{0.67}CO_3$ and (b) $Co_{0.33}Mn_{0.67}CO_3$ precursors.

In order to investigate the thermal behavior of $Mn_{0.33}Co_{0.67}CO_3$ and $Co_{0.33}Mn_{0.67}CO_3$ microspheres, TGA curves of the precursors under atmosphere are shown in Figure S5. The TGA curves could be categorized into two major weight loss processes. The first weight loss below ~ 230 $^{\circ}C$ is attributed to the loss of physical and chemical adsorption on the surface of precursor particles, such as H_2O , HMT and other organic compounds which produced in solvothermal process. The second conspicuous weight loss is due to the thermal decomposition of precursors into

MnCo₂O₄ and CoMn₂O₄, and at the same time, released CO₂ with temperature increasing. For Mn_{0.33}Co_{0.67}CO₃ and Co_{0.33}Mn_{0.67}CO₃ precursors, the value of the second weight are 32.89% and 32.27%, respectively, which are very consistent with the theoretical value (32.87% and 33.23%). TGA, together with XRD and IR, confirmed the ingredient of the precursors perfectly. Furthermore, it was also found that the second major weight loss can be divided into three processes because of the different thermal behaviors of MnCO₃ and CoCO₃. The similar phenomenon was also observed in previous works.^[1,2] According to the TGA curves, the optimal temperature for obtaining MnCo₂O₄ and CoMn₂O₄ is carried out at 600 °C.

[1] J. F. Li, S. L. Xiong, X. W. Li, Y. T. Qian, *Nanoscale*, **2013**, 5, 2045.

[2] X. F. Chen, L. L. Zhang, W. X. Zhang, Y. H. Huang, *J. Alloy Comp.*, **2013**, 559, 5.

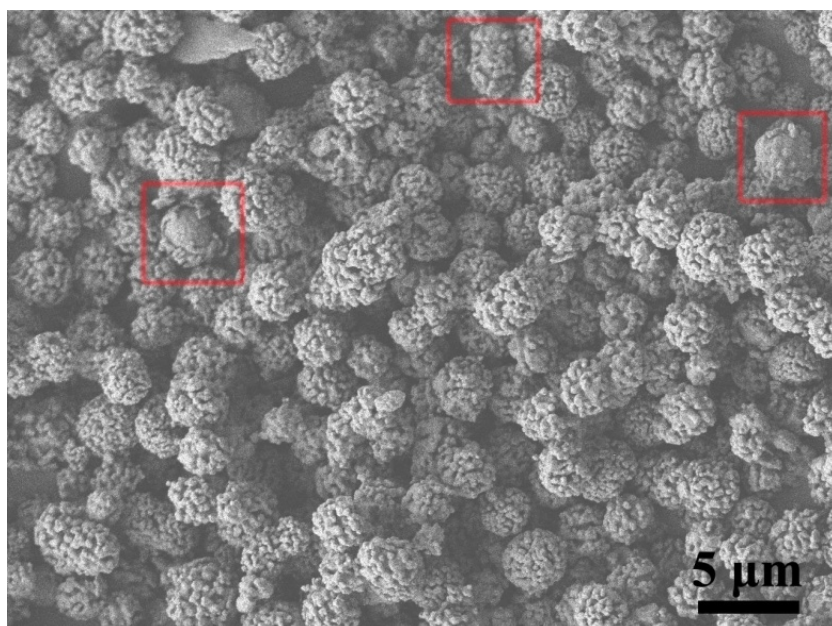


Fig. S7 FESEM image of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ after annealed for 4 h at 600 °C.

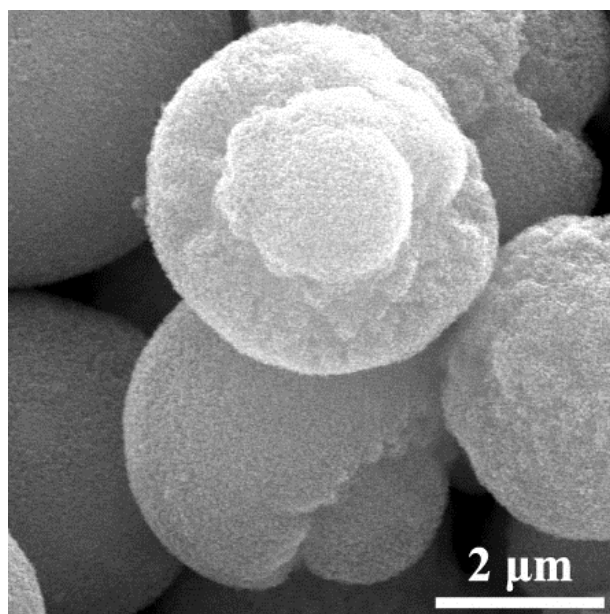


Fig. S8 FESEM image of the broken MnCo_2O_4 microsphere at 600 °C for 6 h.

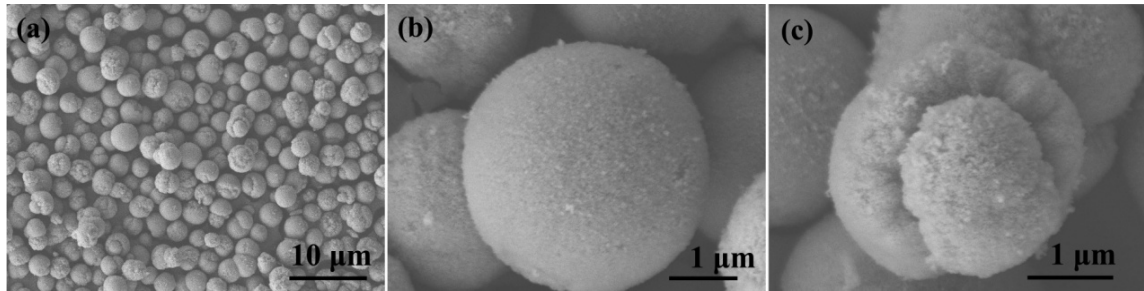


Fig. S9 FESEM image of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ annealed for 10 h at 600 °C.

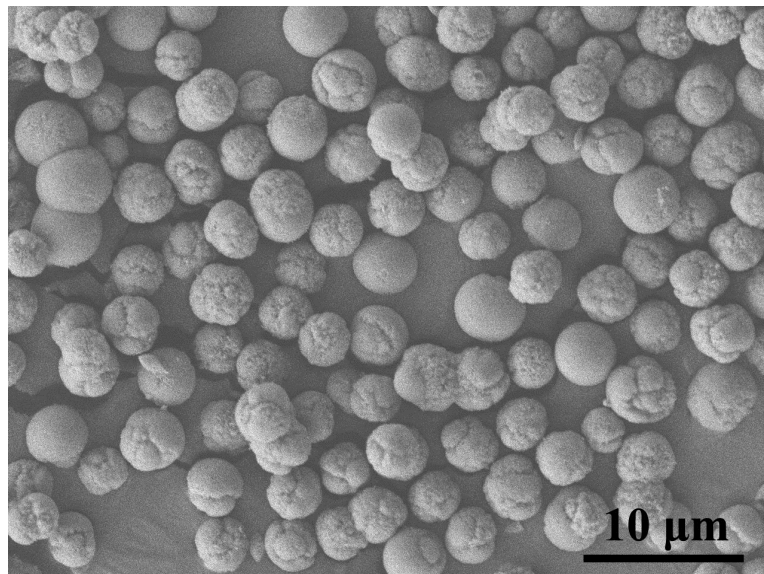


Fig. S10 FESEM image of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ annealed for 12 h at 600 °C.

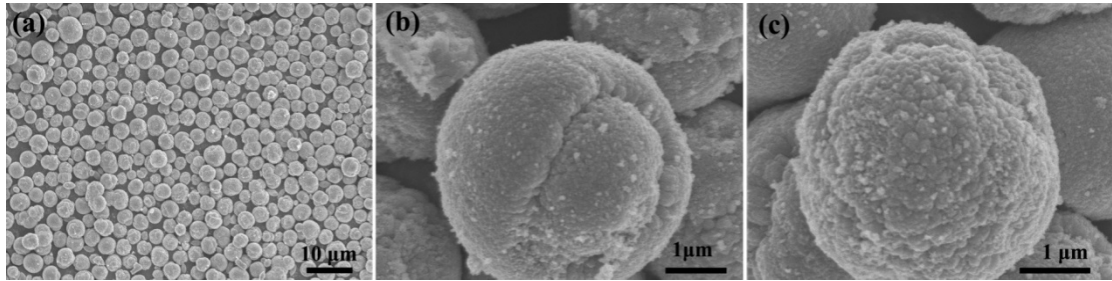


Fig. S11 FESEM image of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ annealed for 16 h at 600 °C.

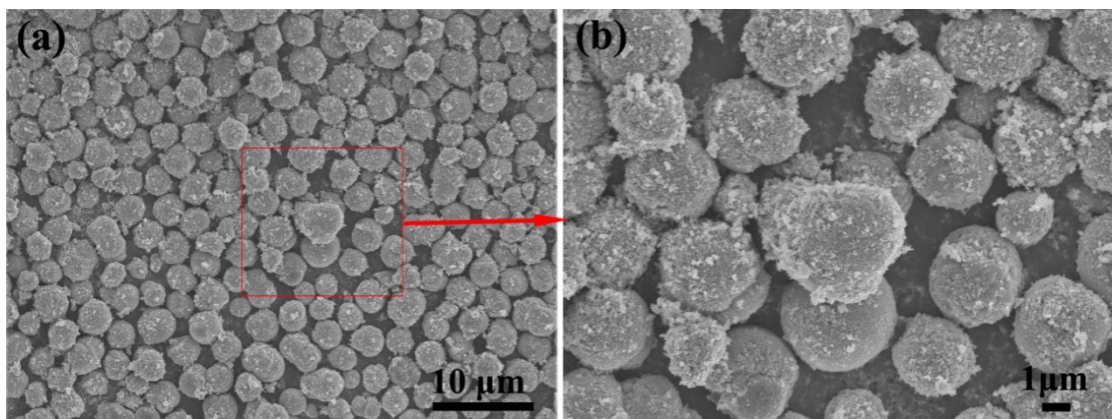


Fig. S12 FESEM image of the $\text{Mn}_{0.33}\text{Co}_{0.67}\text{CO}_3$ annealed for 24 h at 600 °C.

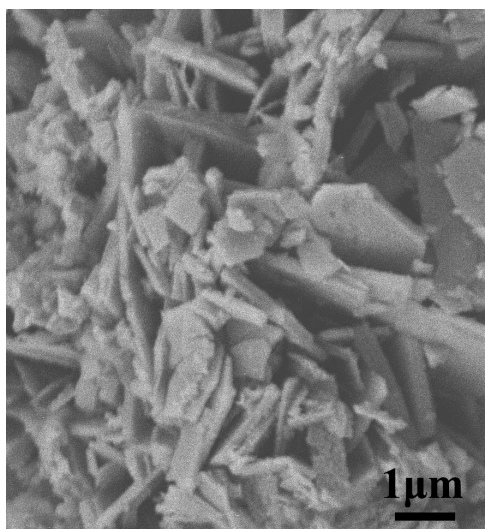


Fig. S13 FESEM image of the product in the absence of HMT in the reaction system.

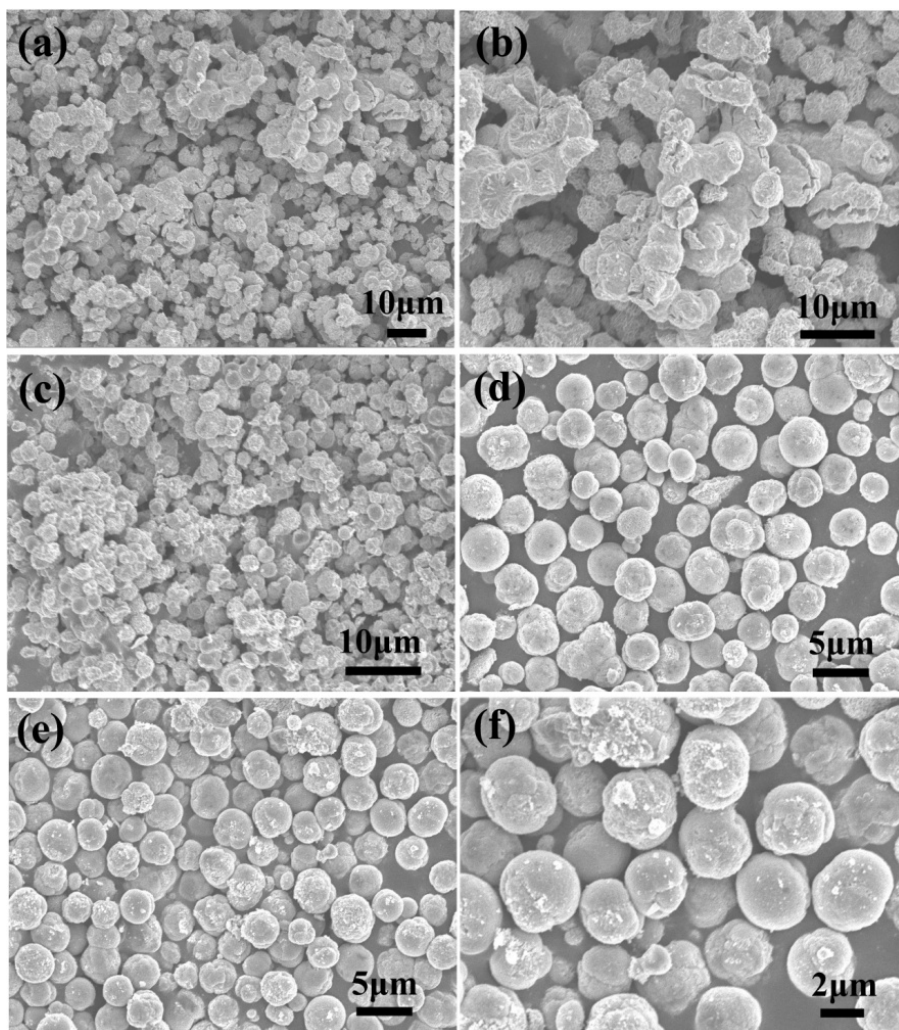
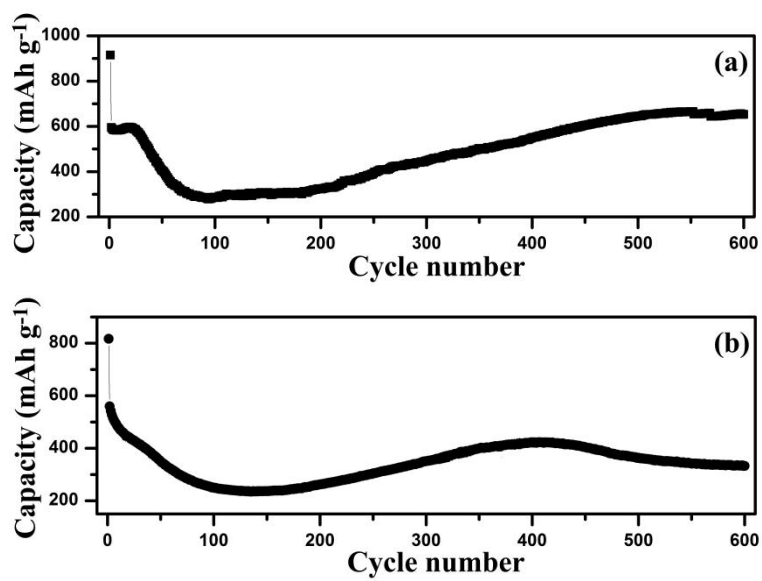


Fig. S14 FESEM images of the products obtained using different masses of HMT: (a,b) 0.1 g; (c) 0.5 g; (d) 3.0 g; (e,f) 5.0 g.



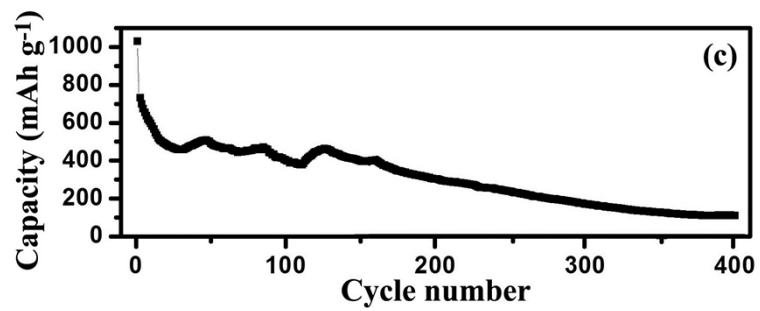


Fig. S15 Cycling performances of the yolk-shell structured (a) MnCo_2O_4 and (b) CoMn_2O_4 microspheres; (c) solid MnCo_2O_4 spheres at 1000 mAh g^{-1} .

Table S1 Morphology change processes of the mesoporous MnCo₂O₄ microspheres at different annealing time.

Sample images	Fig. S2	Fig. 3	Fig. S6	Fig. 5 and S7
Conditions	180 °C 12h	600°C 2 h	600°C 4h	600°C 6h
Morphologies	MnCo-presursor Mn _{0.33} Co _{0.66} CO ₃	Mesoporous MnCo ₂ O ₄ microspheres	Transitional state to forming yolk- shell structure	Yolk-shell microspheres
Sample images	Fig. S8	Fig. S9	Fig. S10	Fig. S11
Conditions	600°C 10h	600°C 12h	600°C 16h	600°C 24h
Morphologies	Broken microspheres	Broken microspheres	Yolk and shell merge together gradually	Solid microspheres

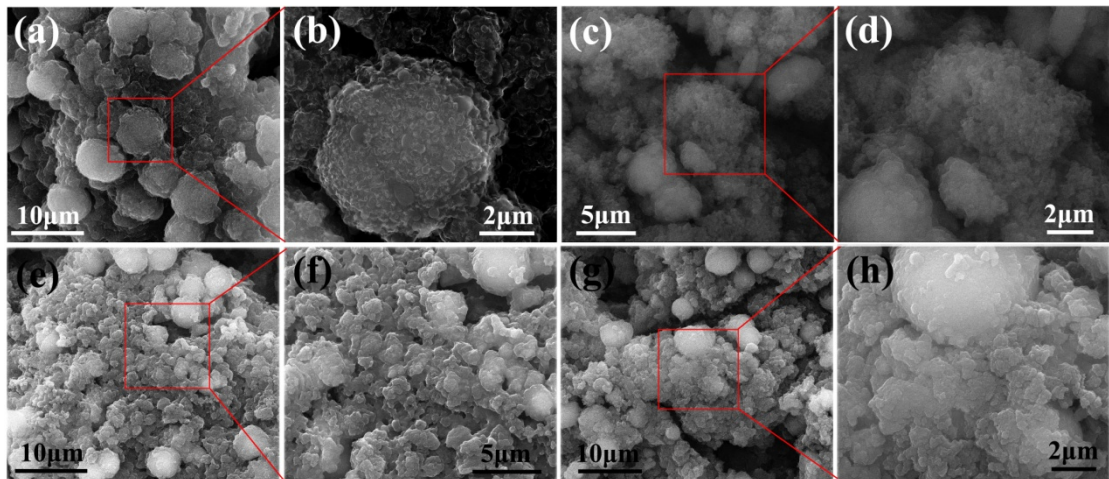


Fig. S16 FESEM images of the porous MnCo₂O₄ and CoMn₂O₄ microspheres after cycles: (a, b) MnCo₂O₄ after 200 cycles; (c, d) CoMn₂O₄ after 200 cycles; (e, f) MnCo₂O₄ after 1000 cycles; (g, h) CoMn₂O₄ after 1000 cycles.

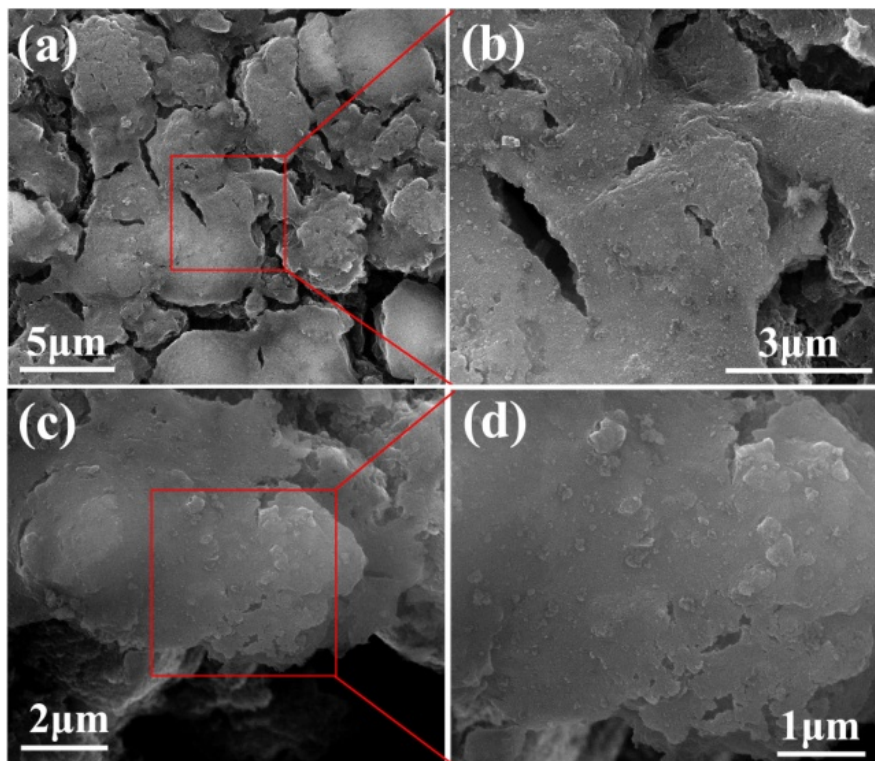


Fig. S17 SEI investigations of the porous (a, b) MnCo₂O₄ and (c, d) CoMn₂O₄ microspheres after 1000 cycles.

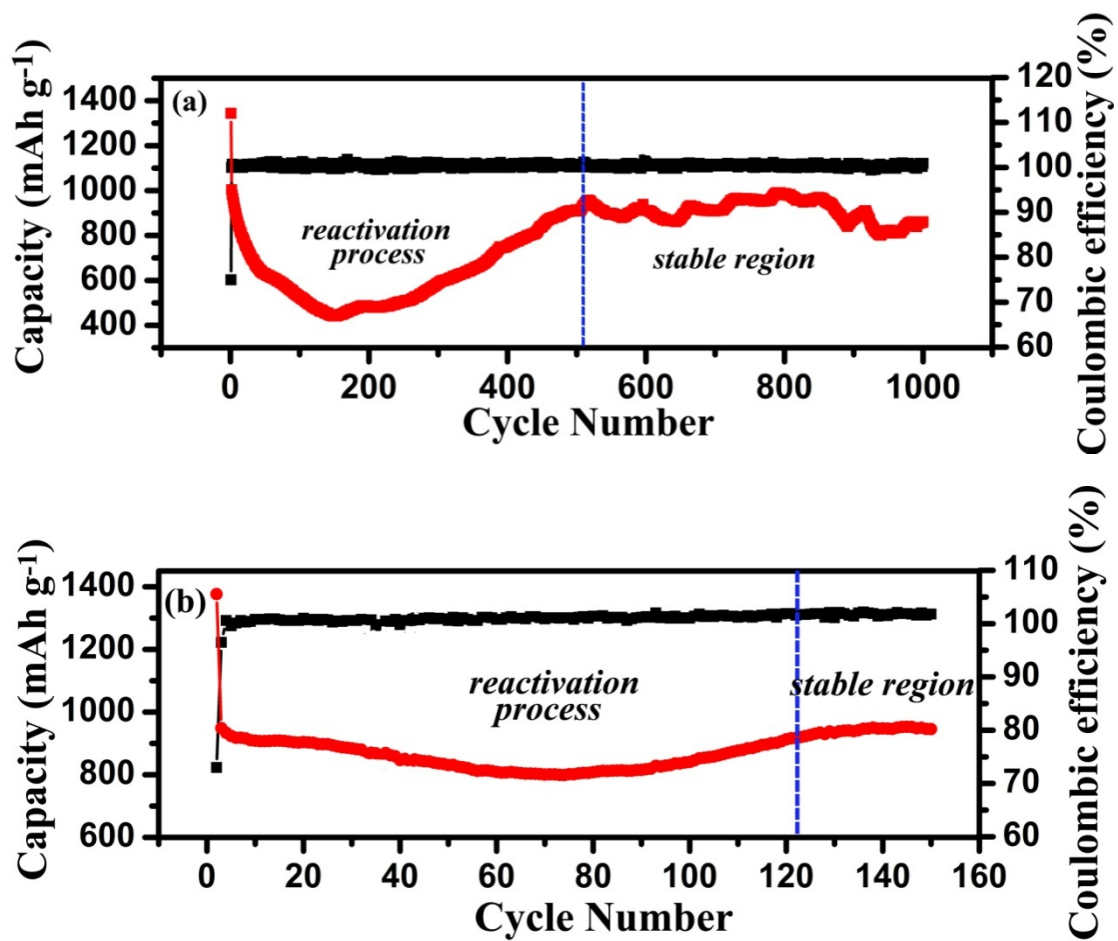


Fig. S18 Cycling performance of the mesoporous MnCo₂O₄ and CoMn₂O₄ microspheres electrode at a current density of 200 mA g⁻¹.

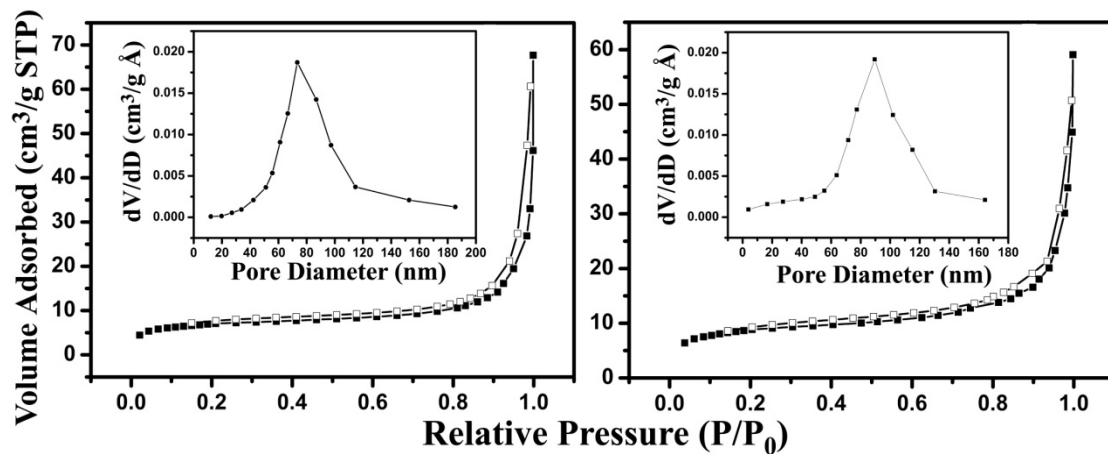


Fig. S19 N_2 adsorption/desorption isotherm and the corresponding pore size distribution of mesoporous $MnCo_2O_4$ and $CoMn_2O_4$ microspheres.

Table S2 Comparison of the cycling performance of MnCo₂O₄ and CoMn₂O₄ between our work and previous reports.

Samples	Current density (mA g ⁻¹)	Cycle number	Reversible capacity (mAh g ⁻¹)	Ref.
MnCo ₂ O ₄ nanowire	200	50	800	1
MnCo ₂ O ₄ microsphere	200	25	722	2
MnCo ₂ O ₄ submicrosphere	400	100	670	3
MnCo ₂ O ₄ quasi-hollow sphere	200	25	755	4
CoMn ₂ O ₄ quasi-hollow sphere	200	25	706	4
MnCo ₂ O ₄ bulks or powders	681	50	400	5
CoMn ₂ O ₄ bulks or powders	691	50	400	5
CoMn ₂ O ₄ hollow microsphere	200	50	624	6
Mn _{1.5} Co _{1.5} O ₄ core-shell microsphere	400	300	618	7
CoMn ₂ O ₄ powder	80	50	330	8
Mesoporous MnCo ₂ O ₄ microsphere	1000	1000	740	This work
Mesoporous CoMn ₂ O ₄ microsphere	1000	1000	420	This work

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