Electronic Supplementary Information

Controlled synthesis of hierarchical $Co_xMn_{3-x}O_4$ array micro-/nanostructures with tunable morphology and composition as integrated electrodes for lithium-ion batteries

Le Yu,[a] *Lei Zhang,*[a] *Hao Bin Wu,*[a] *Genqiang Zhang,*[a] *and Xiong Wen (David) Lou**[a]

[a] School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore, 637459, (Singapore)

Email: xwlou@ntu.edu.sg

Webpage: http://www.ntu.edu.sg/home/xwlou/

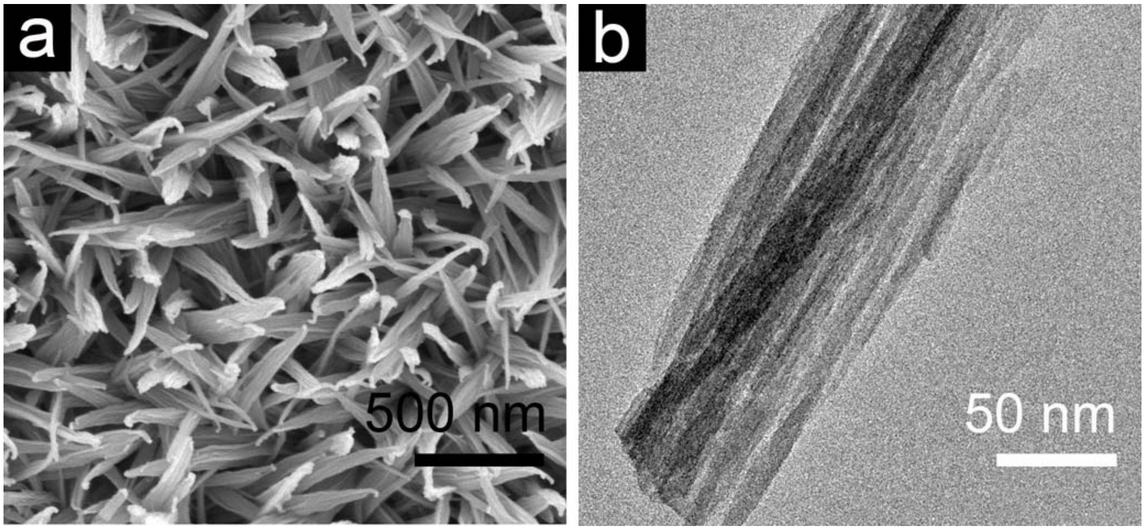


Fig. S1 (a) FESEM image of CMO-0 nanowires array grown on stainless steel foil and (b) TEM image of an individual CMO-0 nanowire.

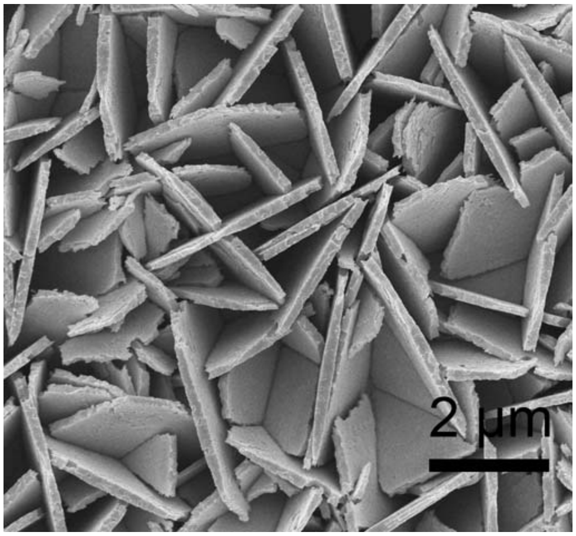


Fig. S2 FESEM image of CMO-50 nanosheets array grown on stainless steel foil.

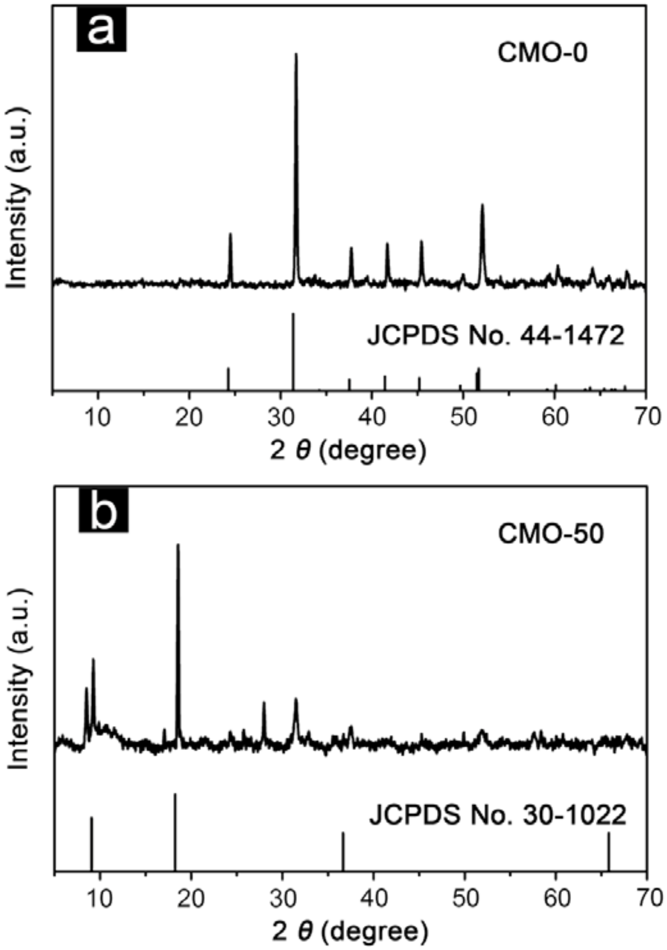


Fig. S3 XRD patterns of (a) hierarchical nanowires (CMO-0) and (b) nanosheets (CMO-50) scratched from stainless steel foil. The X-ray diffraction (XRD) pattern for the typical hierarchical nanowires structure, CMO-0, can be assigned to the $Co_{0.33}Mn_{0.67}CO_3$ (JCPDS card no. 44-1472). Meanwhile, the main phase of the typical hierarchical nanosheets structure, CMO-50, can be assigned to (Co, Mn)OOH (JCPDS card no. 30-1022).

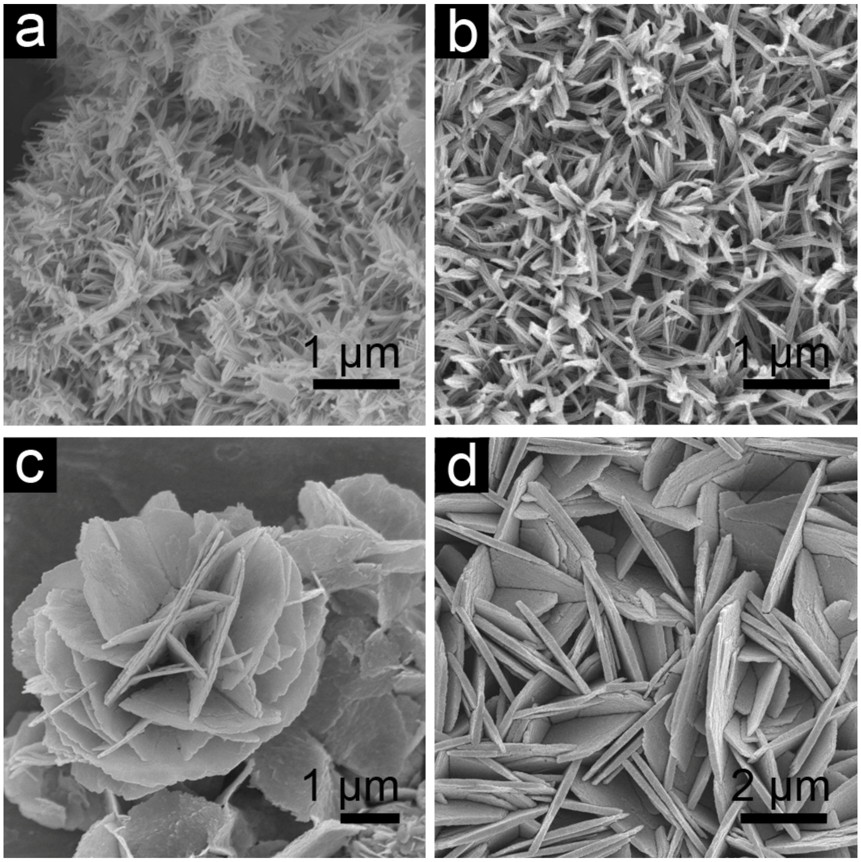


Fig. S4 FESEM images of Co-Mn precursor structures obtained without substrate (a, c) and on the surface of Ti foil (b, d).The synthesis solvent for (a, b) is water. Meanwhile, the synthesis solvent for (c, d) is the mixed solvent of EtOH/H_2O (50mL/30mL).

In order to investigate the role of substrate in the formation of these nanostructures, further experiments have been carried out without the help of stainless steel substrate. Besides, Ti foil has been also applied as the substrate to synthesis these nanostructures with exactly the same reaction conditions. The synthesis of the nanowires and nanosheets precursors are not affected much by Ti foil or in the absence of the substrate. Hierarchical nanowires can still be formed in DI water. Meanwhile, uniform nanosheets structure could also be found in the mixture of ethanol and water. From the results above, we can deduce that the driving force for the variation in morphology of these nanostructures is the alteration of solvent compositions. The introduction of substrate does not affect the formation of these nanostructures in this case. The stainless steel or Ti foil simply serves as an inert substrate to allow the heterogeneous growth of Co-Mn precursor nanostructures.

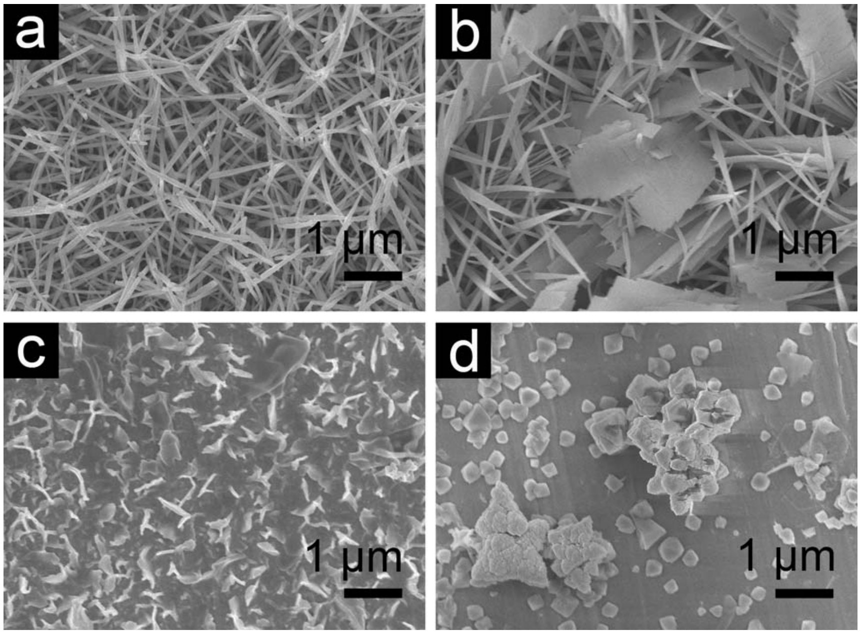
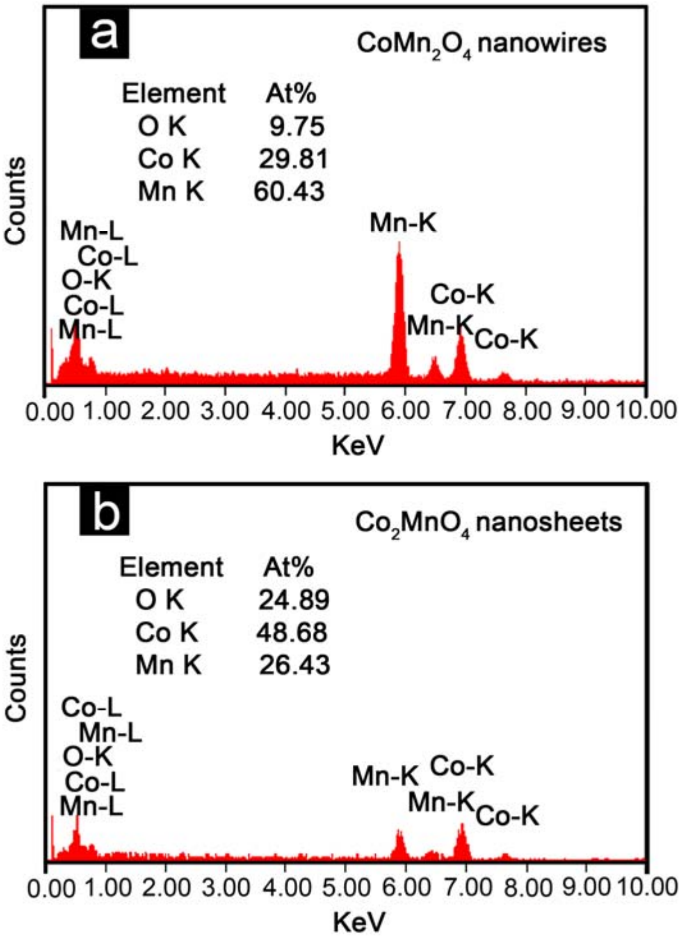


Fig. S5 Co-based structures obtained using the mixed solvent of EtOH/H_2O (50mL/30mL) (a), and water as the solvent (b). Mn-based structures obtained using the mixed solvent of EtOH/H_2O (50mL/30mL) (c), and water as the solvent (d).



Element	At%
O K	9.75
Co K	29.81
Mn K	60.43

Element	At%
O K	24.89
Co K	48.68
Mn K	26.43

Fig. S6 EDX spectra of (a) hierarchical $CoMn_2O_4$ nanowires and (b) $MnCo_2O_4$ nanosheets scratched from stainless steel foil.

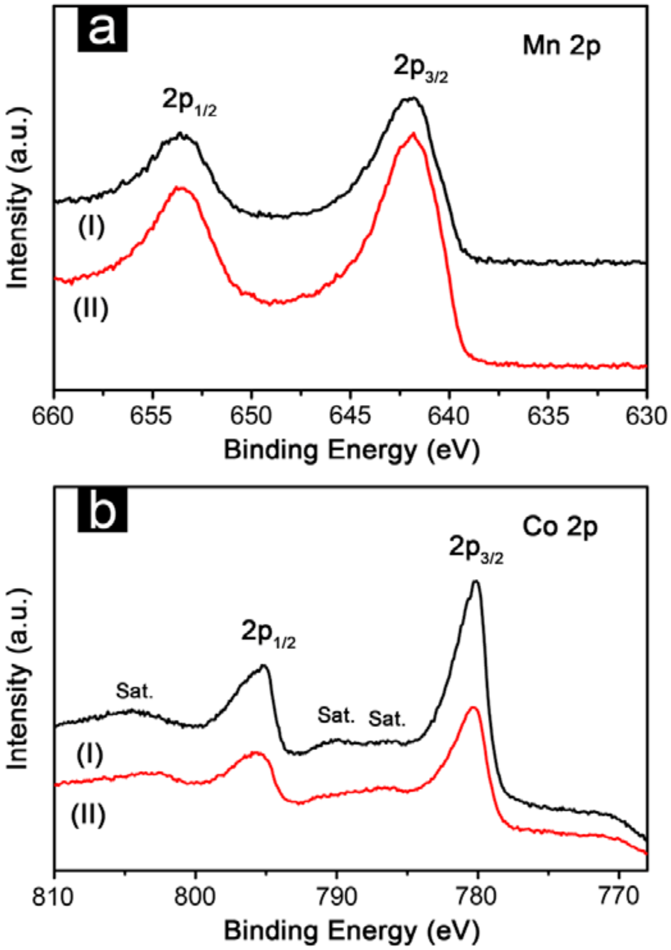


Fig. S7 XPS spectra of (a) Mn 2p, (b) Co 2p for the hierarchical $CoMn_2O_4$ nanowires (in black line) and $MnCo_2O_4$ nanosheets (in red line) grown on stainless steel foil.

The Mn 2p spectrum of $CoMn_2O_4$ features two main spin-orbit lines of $2p_{3/2}$ at 642.2 eV and $2p_{1/2}$ at 653.6 eV. Meanwhile, for the $MnCo_2O_4$, the Mn 2p spectrum also shows two major peaks with binding energies (BE) values at 642.0 and 653.5 eV, assigned to the Mn $2p_{3/2}$ and Mn $2p_{1/2}$ peaks, respectively. Both Mn 2p spectra can be assigned to the existence of Mn^{2+} and Mn^{3+} cations.[1] The Co 2p spectra for both $CoMn_2O_4$ and $MnCo_2O_4$ also consist of two spin-orbit doublets and three shakeup satellites (denoted as “Sat.”), characteristic of Co^{2+} and Co^{3+} cations.[2] These data show that the surface of the as-prepared $CoMn_2O_4$ or $MnCo_2O_4$ samples belongs to the mixed valence compound, which has a composition containing Mn^{2+}, Mn^{3+}, Co^{2+} and Co^{3+}.

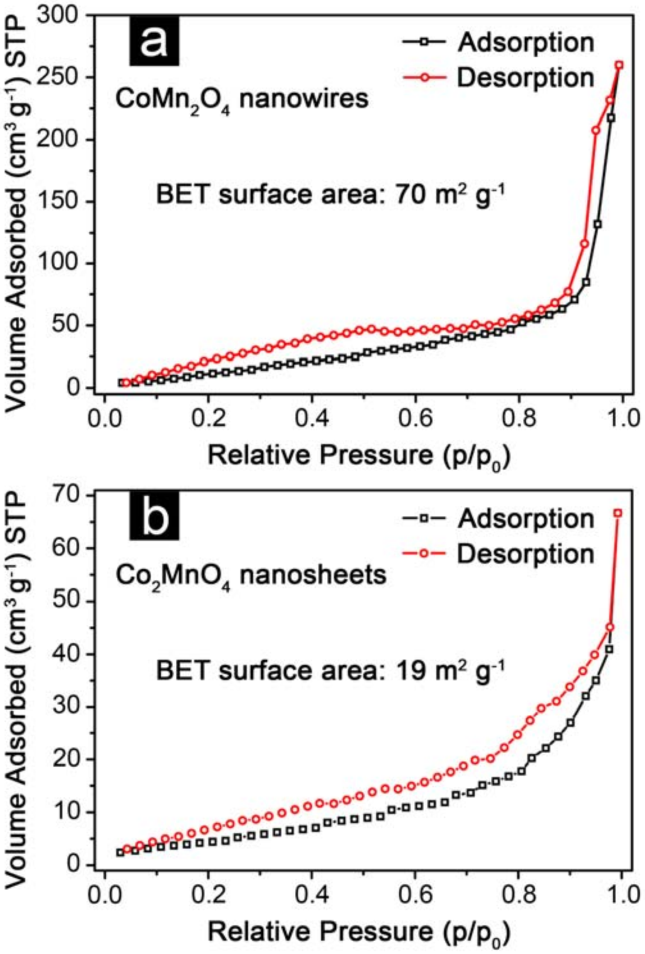


Fig. S8 N_2 adsorption-desorption isotherms at 77 K of (a) hierarchical $CoMn_2O_4$ nanowires and (b) $MnCo_2O_4$ nanosheets scratched from stainless steel foil.

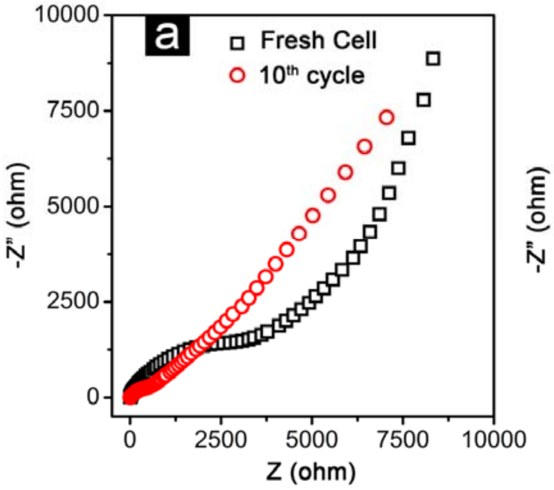


Fig. S9 Nyquist plots of (a) hierarchical $CoMn_2O_4$ nanowires and (b) $MnCo_2O_4$ nanosheets grown on stainless steel foil before discharge process (in black squares) and after charging/discharging for 10 cycles (in red circles).

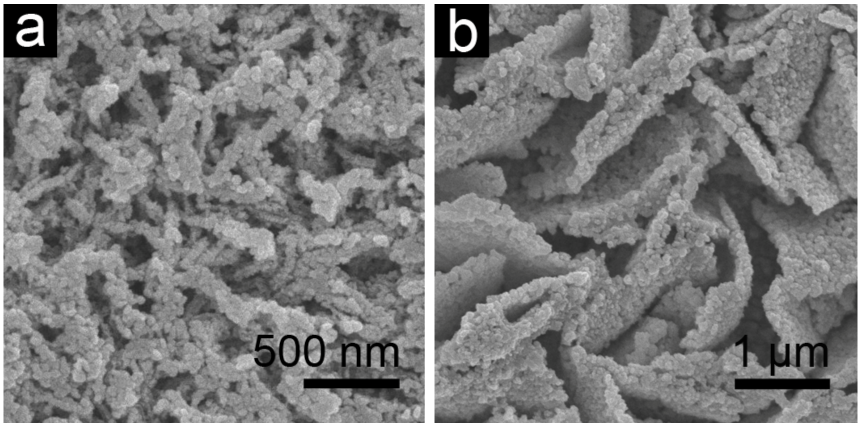


Fig. S10 FESEM images of $Co_xMn_{3-x}O_4$ nanostructures after 10 discharge-charge cycles at 800 mA g^{-1}. (a) $CoMn_2O_4$ nanowires and (b) $MnCo_2O_4$ nanosheets grown on stainless steel foil.

References

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

2. S. L. Xiong, J. S. Chen, X. W. Lou and H. C. Zeng, *Adv. Funct. Mater.*, 2012, **22**, 861.