Supporting Information

MnCo$_2$O$_4$ Decorated Magnéli Phase Titanium Oxide as a Carbon-Free Cathode for Li-O$_2$ Batteries

Xuecheng Cao$^a$, Zhihui Sun$^a$, Xiangjun Zheng$^a$, Jinghua Tian$^a$, Chao Jin$^a$, Ruizhi Yang$^a$,* Fan Li$^b$, Ping He$^{c,*}$, Haoshen Zhou$^{c,d,*}$

$^a$Soochow Institute for Energy and Materials InnovationS, College of Physics, Optoelectronics and Energy & Collaborative Innovation Center of Suzhou Nano Science and Technology

Soochow University

Suzhou 215000, P. R. China

$^b$College of Environmental & Energy Engineering

Beijing University of Technology

Beijing 100124, P. R. China

$^c$Center of Energy Storage Materials and Technology, College of Engineering and Applied Sciences, National Laboratory of Solid State Microstructures, Collaborative Innovation Center of Advanced Microstructures

Nanjing University

Nanjing 210093, P. R. China

$^d$Energy Technology Research Institute

National Institute of Advanced Industrial Science and Technology (AIST)

Tsukuba 3058568, Japan

E-mails: yangrz@suda.edu.cn; pinghe@nju.edu.cn; hs.zhou@aist.go.jp
The determination of weight ratio of MCO to Ti$_4$O$_7$ for Ti$_4$O$_7$/MCO:

Because Ti$_4$O$_7$ is very hard to dissolve in acid media, the Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) can not be directly used to determine the weight ratio of MCO and Ti$_4$O$_7$. Therefore, we have designed an experiment to ensure the precise weight ratio of MCO and Ti$_4$O$_7$ for Ti$_4$O$_7$/MCO hybrid sample to be obtained. Firstly, 0.0153g of Ti$_4$O$_7$/MCO hybrid was dispersed in 20 mL of 1M H$_2$SO$_4$ solution and stirred for 10 h. In this process, MCO dissolved in acidic solution while Ti$_4$O$_7$ remained as checked by ICP-OES. This process was repeated several times to ensure that MCO dissolved in acidic solution completely by being checked by the ICP-OES. Then the centrifugation and washing were taken to separate Ti$_4$O$_7$ from the solution. After freeze-drying, the weight of Ti$_4$O$_7$ was 0.0123g. So, the weight ratio of MCO is $w_{\text{MCO}} = (0.0153 - 0.0123) / 0.0153 = 19.6$ wt.%, the weight ratio of Ti$_4$O$_7$ is $w_{\text{MCO}} = 0.0123 / 0.0153 = 80.4$ wt%.
Figure S1. SEM image of Ti₄O₇@SiO₂ after H₂ reduction process.

Figure S2. SEM image of Ti₄O₇ particles synthesized without the protection of SiO₂.
Figure S3. SEM elemental mapping of Ti$_4$O$_7$/MCO hybrid.

Figure S4. Cycling performance of C+MCO electrode.
Figure S5. (a) Raman spectra of the pristine (black), discharged (red) and recharged (blue) Ti$_4$O$_7$/MCO cathode. (b) The enlarged Raman spectrum of Ti$_4$O$_7$/MCO cathode in the black box of (a)