Electronic Supplementary Information (ESI)

Self-assembled porous hierarchical-like CoO@C microsheets transformed from inorganic-organic precursors and their lithium-ion battery application

Jun Liu,^a Yichun Zhou,^{*a} Chunping Liu,^a Jinbin Wang,^a Yong Pan^a and Dongfeng

Xue^{*bc}

^aKey Laboratory of Low Dimensional Materials & Application Technology, Ministry

of Education, Faculty of Materials, Optoelectronics and Physics, Xiangtan University,

411105, China.

Fax: (+) 86-731-58293586; Tel: (+) 86-731-58298119;

E-mail: zhouyc@xtu.edu.cn

^bSchool of Chemical Engineering, Dalian University of Technology, Dalian, 116024, China;

^cState Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China. E-mail: dongfeng@ciac.jl.cn XRD pattern of inorganic-organic precursors



Fig. S1 XRD pattern of inorganic-organic precursors, which clearly shows that these uniform self-assembled hierarchical-like Co(OH)₂–DS microsheets are of high-crystallized.

SEM images of precursors in the absence of SDS



Fig. S2 SEM images of $Co(OH)_2$ precursors obtained in the absence of structure-directing SDS, which clearly shows that these precursors were crystallized in the shape of plate-like morphology. However, these nonuniform micro/nanoplates failed to self-assemble into hierarchical-like microsheets due to the absence of intercalated organic molecule SDS between $Co(OH)_2$ layers.

TGA plot of hierarchical CoO@C microsheets

The TGA plot in air shows a weight loss of 1.9% up to 240 °C is attributed the release of water absorbed on the sample, and weight gain of 1.6% in the range of 240–380 °C is believed to correspond the oxidation of CoO in air. In a typical thermogravimetric process in air for CoO, the CoO can be oxidized to Co_3O_4 with a weigh gain of 7.1%, based on completely oxidation of CoO. At about 400 °C, the carbon content in the samples starts to be oxidized to CO_2 gas making the mass of the sample decreases slowly. The total weight loss in the TGA curves is 9.5%, in which the weight loss of adsorbed water is 1.9%, and thus the carbon content is calculated to be 14.7% (7.6% + 7.1%).



Fig. S3 TGA curve of self-assembled porous hierarchical-like CoO@C microsheets in air.

SEM images of precursor obtained at 220 °C

We have prepared samples at other different hydrothermal conditions. For example, when the hydrothermal crystallization temperature was 220 °C or higher temperature, DS-intercalated $Co(OH)_2$ products were not achieved. And we only got dehydrated oxide Co_3O_4 products. Fig. S5 exhibit the morphology of these Co_3O_4 products. From these SEM images, it can be seen that these Co_3O_4 products have a uniform cubic shape with an average diameter of about 1 µm.



Fig. S4 SEM images of Co_3O_4 microcubes obtained at 220 °C, which show a uniform cubic shape with an average diameter of about 1 μ m.

SEM images of products calcinated at 700 °C

The calcination temperature has an important effect on the microstructure and composition of the final products during the annealing process. When the calcination temperature is below 550 °C, for example, at 450 °C the inorganic–organic Co(OH)₂–DS precursors were not completely converted into inorganic CoO@C products, and partial organic DS were residual, which can degrade the electrochemical performance of final electrode materials. However, when the calcination temperature is too high, such as at 700 °C partial hierarchical-like CoO@C microsheets collapsed during the chemical transformation process. Fig. S5 shows SEM image of the collapsed hierarchical-like CoO@C microsheets after annealing at 700 °C.



Fig. S5 SEM images of the collapsed hierarchical-like CoO@C microsheets after annealing at 700 °C.

SAED patterns of porous CoO@C microsheets

The SAED patterns show continuous ring patterns without any rings of secondary phases revealing their polycrystalline structure. However, the little diffusive SAED ring pattern identifies that these CoO@C microsheets are of low-crystallized, which is consistent with the XRD results.



Fig. S6 TEM image and SAED patterns (the inset) of porous hierarchical-like CoO@C microsheets, which clearly show that these porous microsheets are polycrystalline.

Discharge-charge voltage profiles and the corresponding differential capacity versus voltage plots

Fig. S7a and S7c show the 1st-cycle discharge-charge voltage profiles at the 0.2C rate for hierarchical-like CoO@C microsheets and CoO microsheets, respectively. The corresponding differential capacity versus voltage plots are shown in Fig. S7b and S7d, respectively. For hierarchical-like CoO@C microsheets, during the first lithiation process, one distinct intensive peak can be observed at 1.12 V, which is ascribed to the lithiation process. For bare CoO microsheets, two distinct peaks (at 0.73 and 0.94 V) are reversible, which can be attributed the lithiation with different site energies.



Fig. S7 The 1st-cyle discharge-charge voltage profiles of porous hierarchical-like CoO@C microsheets (a) and bare CoO microsheets (b) at a 0.2C rate. The corresponding differential capacity versus voltage plots are shown in Fig. S7b and S7d, respectively.